

Development and Applications of an Orbital Phase Theory for Noncyclic Systems

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Koji Iwase

Preface

Control of stabilities is necessary for designing molecules or chemical reactions. Orbital phase theories have been applied to the cyclic structures which involve cyclic orbital interactions. This is the case with the $4n+2\pi$ electron rule for the aromaticity and the stereoselection rule for the pericyclic reactions. Cyclic orbital interactions were recently shown to be involved even in noncyclic structures and to control the stabilities. In this thesis the orbital phase theory was applied to noncyclic systems of closed-shell electronic structures to give novel predictions of stabilities and reactivities. The stability control of open-shell electronic structures is also required in some fields, e.g., photochemistry, molecular magnetic materials. An orbital phase theory for the open-shell systems was developed. The extended theory was applied to the relative stabilities of diradical isomers in both singlet and triplet states, and to the spin preferences of ground states of diradicals. This thesis includes the following chapters 1-7.

In Chapter 1 the thermodynamic relative stability between cross and linear conjugated isomers of carbanions derived from enamines or vinyl ethers was predicted by the or-

bital phase theory. The prediction was confirmed experimentally. In Chapter 2 electron localizing and delocalizing non-cyclic conjugated polyion and related compounds were designed by the orbital phase theory. In Chapter 3 the orbital phase continuity-discontinuity properties was proposed to depend on the number of electrons. This was applied to the cross and linear conjugations, i. e., substituted vinyl carbenes and biscarbenes. The theory was applied to tricoordinated metal complexes (ML_3) in Chapter 4. The noncyclic L-M-L structures were shown to involve the cyclic orbital interactions. The orbital phase properties require the L-M-L angles to be abnormally acute. This was confirmed by the ab initio calculations.

A phase theory was developed for the open-shell systems in Chapter 5 and 6. The theory was applied to predict the thermodynamic relative stabilities of isomers of diradicals in both singlet and triplet states. In Chapter 6 the theory was applied to predict spin multiplicities of ground states of the diradicals.

Molecules can be destabilized thermodynamically or kinetically. Both factors should be considered for designing molecules. Cyclic polyenes have, however, been discussed from a thermodynamic point of view or in terms of the Hückel rule or the resonance energy. In Chapter 7 the kinetic instabilities of cyclic polyenes toward electron donors and acceptors were predicted by the orbital phase theory.

Acknowledgments

I would like to express my sincere gratitude to Professor Satoshi Inagaki for his enlightening discussions and continual encouragement. His enthusiasm in organic and quantum chemistry has played a major role in the motivation and direction of my interests. Grateful acknowledgment is made to Professor Masaru Ishida and Dr. Yuji Naruse for their valuable discussions and advises. I would like to express my appreciation to Professor Shingo Sakai of Osaka Sangyo University, Mr. Hirofumi Kawata, and Mrs. Naomi Nagata for their active collaborations and discussions, and to the students of our laboratory for their help.

It is also my great pleasure to thank Professor Emeritus Yoshio Hirabayashi for his advises and Professor Shinji Kato for his encouragement.

I would like to thank Professor Paul von Ragué Schleyer of Universität Erlange-Nürnberg for private communication of their results in prior to publication and for stimulating criticism on the manuscript of Chapter 2. Professor Hideo Tomioka of Mie University is also acknowledged for valuable informations on vinylcarbenes in Chapter 3.

Ab initio molecular orbital calculations were carried out

on the HITAC-M200H computer, at the Institute for Molecular Science, with the IMSPACK and the GAUSSIAN80 programs, and on the IBM RISC SYSTEM/6000 computer, with the GAUSSIAN92 program. The other calculations were carried out on the FACOM-M382 computer, at Nagoya University Computer Center.

I would like to thank SAKATA INX Corp., especially Managing Director Mr. Hirohito Kenmochi and General Manager Mr. Hiroshi Ohta for giving the opportunity for the investigations.

Finally, I would like to express my sincere gratitude to my parents for their understanding and continual encouragement.

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Chapter 1

Theoretical Prediction and Experimental Confirmation of Relative Stabilities of Isomeric Allyl Anions from Enamines and Vinyl Ethers

Abstract: Relative stabilities of isomeric allyl anions from enamines and vinyl ethers are predicted in terms of the continuity–discontinuity of the orbital phase. The predictions are supported by ab initio molecular orbital calculations and confirmed by experiments on model compounds.

Carbanions from enamines have been used as synthetic reagents for carbon–carbon bond formation.¹ Enamines can give rise to 1- and 2-aminoallyl anions. The relative stabilities of these isomeric species should determine the regioselectivity of subsequent alkylation reactions. Recently, cyclic orbital interaction was found to be involved in noncyclic conjugation.² Noncyclic delocalization of electrons is under control of the orbital phase properties, as is cyclic

delocalization.

In this chapter we predict the stabilities in terms of orbital phase, carry out geometry optimization by ab initio molecular orbital calculations, and examine the prediction by experiments.

Results

Orbital Phase prediction. Aminoallyl anions are considered to be composed of a double bond and lone pairs of electrons on an anionic center and a nitrogen atom. The mechanism of electron delocalization among the three systems is illustrated in Figure 1. Electron shifts from both lone pairs to the double bond involve the interactions between the nonbonding orbitals (n_C and n_N) and the antibonding orbital (π^*). The resulting electron holes in the anionic center and in nitrogen can be supplied with an electron from the double bond through the interactions of the nonbonding orbitals with the bonding orbital (π) (Figure 1a). As a result, the delocalization process contains cyclic orbital interaction between the n_C , π^* , n_N , and π orbitals (Figure 1b). The orbital phase conditions for delocalization² are: (1) electron donating orbitals out of phase, (2) electron accepting orbitals in phase, and (3) donating and accepting orbitals in phase. The cyclic orbital interaction that simultaneously satisfies these three requirements promotes delocalization. The systems that contain such an orbital interaction are electron

delocalizing or stable. The others are electron localizing or unstable. Application of these conditions leads to the prediction that the 2-aminoallyl anion is electron delocalizing (Figure 1c) whereas the 1-aminoallyl anion is electron localizing (Figure 1d).

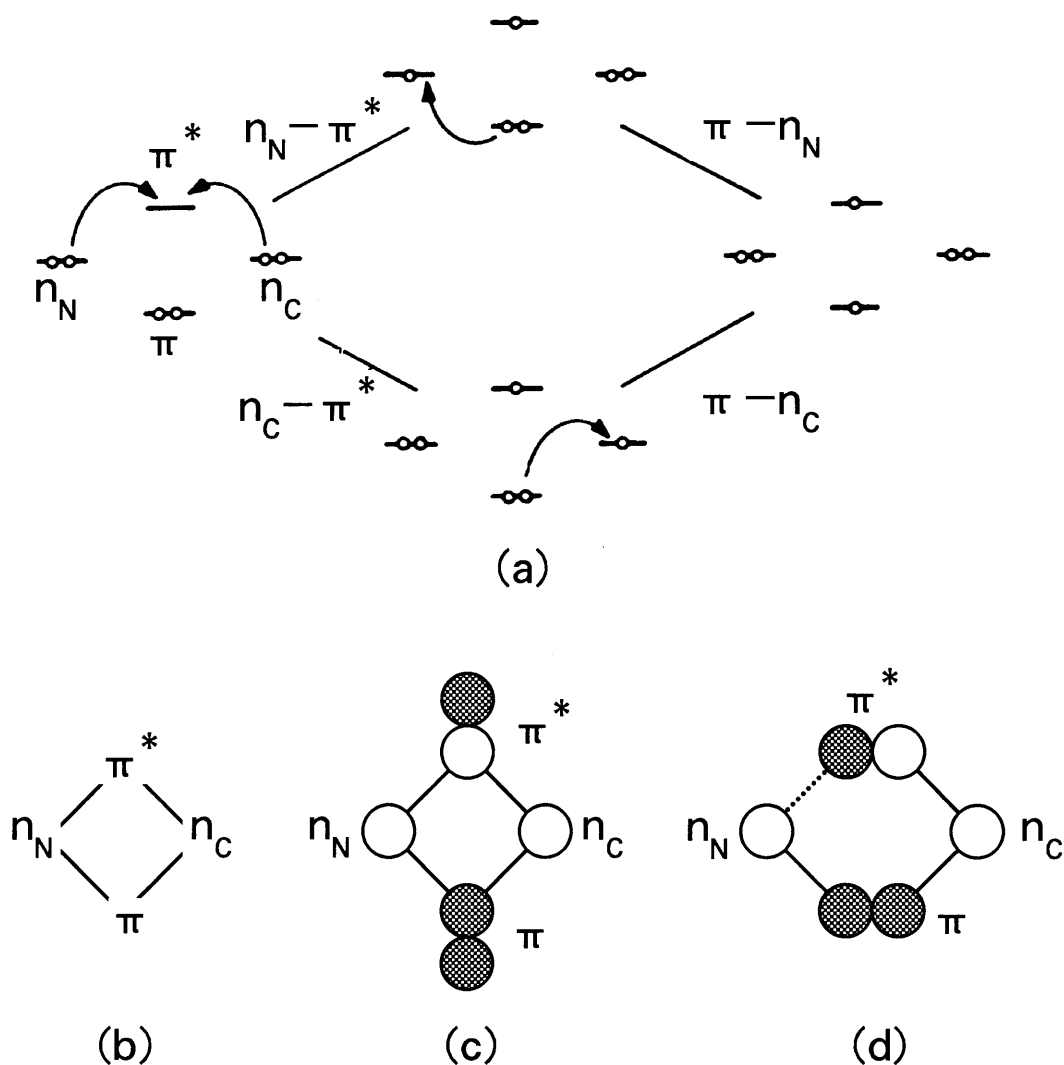


Figure 1. Electron delocalization in aminoallyl anions. (a) Mechanism; (b) cyclic orbital interaction; (c) orbital phase continuity in cross conjugation; and (d) discontinuity in linear conjugation.

Geometry Optimization. Molecular geometries of aminoallyl anions were optimized by ab initio molecular orbital calculations with an STO-3G basis set. The first of the constrained geometries subjected to the optimization was the π -planar model with all atoms in the same plane (Figure 2). Under the constraint the 1-aminoallyl anion belongs to the C_s point group and the 2-aminoallyl anion to the C_{2v} . In the second geometry, the constraint is partially relaxed: the pyramidization at the nitrogen is allowed. Interaction between the allyl anion and the nitrogen lone pair electrons is weakened but still remains to an appreciable extent. In this π -pyramidal model the 1-aminoallyl anion has no symmetry constraint, and the 2-aminoallyl anion belongs to the C_s point group. In the last model, the nonbonding orbital lies

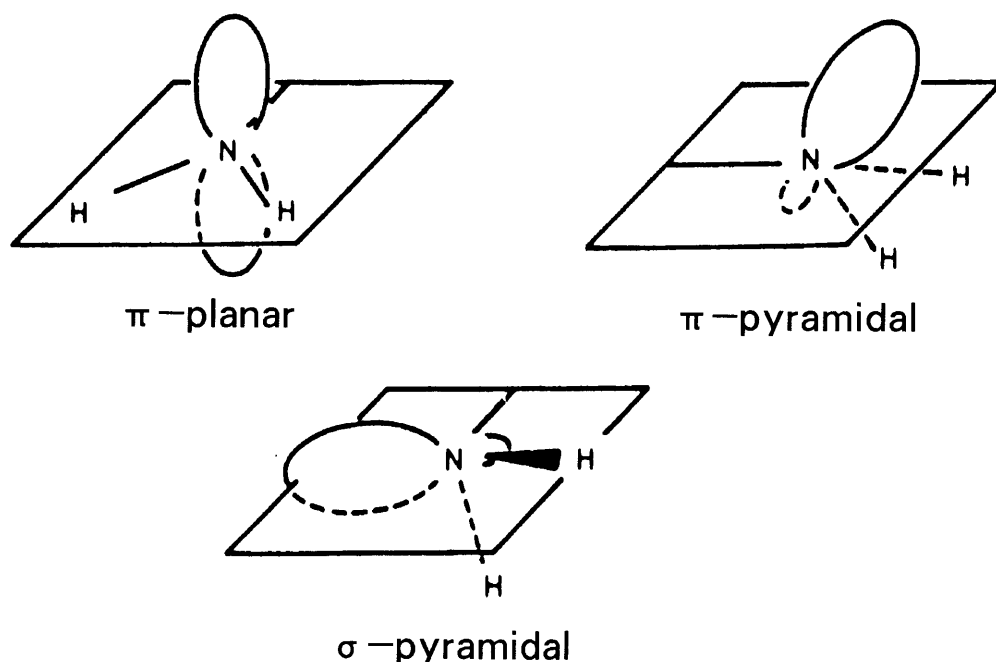


Figure 2. Models for geometry optimization.

in the σ -plane, and the pyramidization is allowed. There is no overlap interaction between the lone pair electrons and the allyl π -systems. Both anions belong to the C_s point group in this σ -pyramidal model.

The orbital phase prediction of the relative stabilities was born out by ab initio molecular orbital calculations (Table 1). The 2-aminoallyl anion was found to be more stable than the 1-aminoallyl anion as far as the overlap interaction between the nonbonding orbital on nitrogen and the π -orbitals was concerned (π -models). The calculations with 4-31G basis set on STO-3G optimized geometries also confirmed the relative stabilities. The most stable model of the 2-aminoallyl anion is a π -model (planar or pyramidal). This is also consistent with the prediction that the 2-aminoallyl anion with the π -type interaction between the allyl and amino moieties is electron delocalizing. It is worth noting that the most stable conformer of the 1-aminoallyl anion is σ -pyramidal. This result could be expected from the prediction that the conjugation that includes the lone pairs of electrons in the 1-aminoallyl anion is electron localizing.

The optimized geometries also support the orbital phase prediction. In the π -planar models the C-N bond length is shorter in 2-aminoallyl anion than in the 1-aminoallyl (Figure 3). This is interpreted as being the result of electron delocalization between allyl and amino moieties. The lone pairs of electrons can delocalize to a greater extent in the electron delocalizing 2-aminoallyl anion. The significant bond alternation in the 1-aminoallyl anion may be due to the

Table 1. Relative Energies of Aminoallyl Anions (kcal/mol)

anion	model	relative energy ^a	
		STO-3G/STO-3G	4-31G/STO-3G
2-aminoallyl	π -planar (C_{2v})	+9.08	0.00
	π -pyramidal (C_s)	0.00	+1.45
	σ -pyramidal (C_s)	+4.56	+6.43
1-aminoallyl	π -planar (C_s)	+24.38	+19.77
	π -pyramidal (C_1)	+3.45	+9.25
	σ -pyramidal (C_s)	+3.28	+8.80

^aThe reference is the total energy of the most stable model.

localization. The π -pyramidal model of the 1-aminoallyl anion, which has no symmetry constraint, is optimized to have almost the same geometry as the σ -pyramidal model. This is a result of the reluctance of the nitrogen lone pair of electrons to conjugate with the allyl system in the localization.

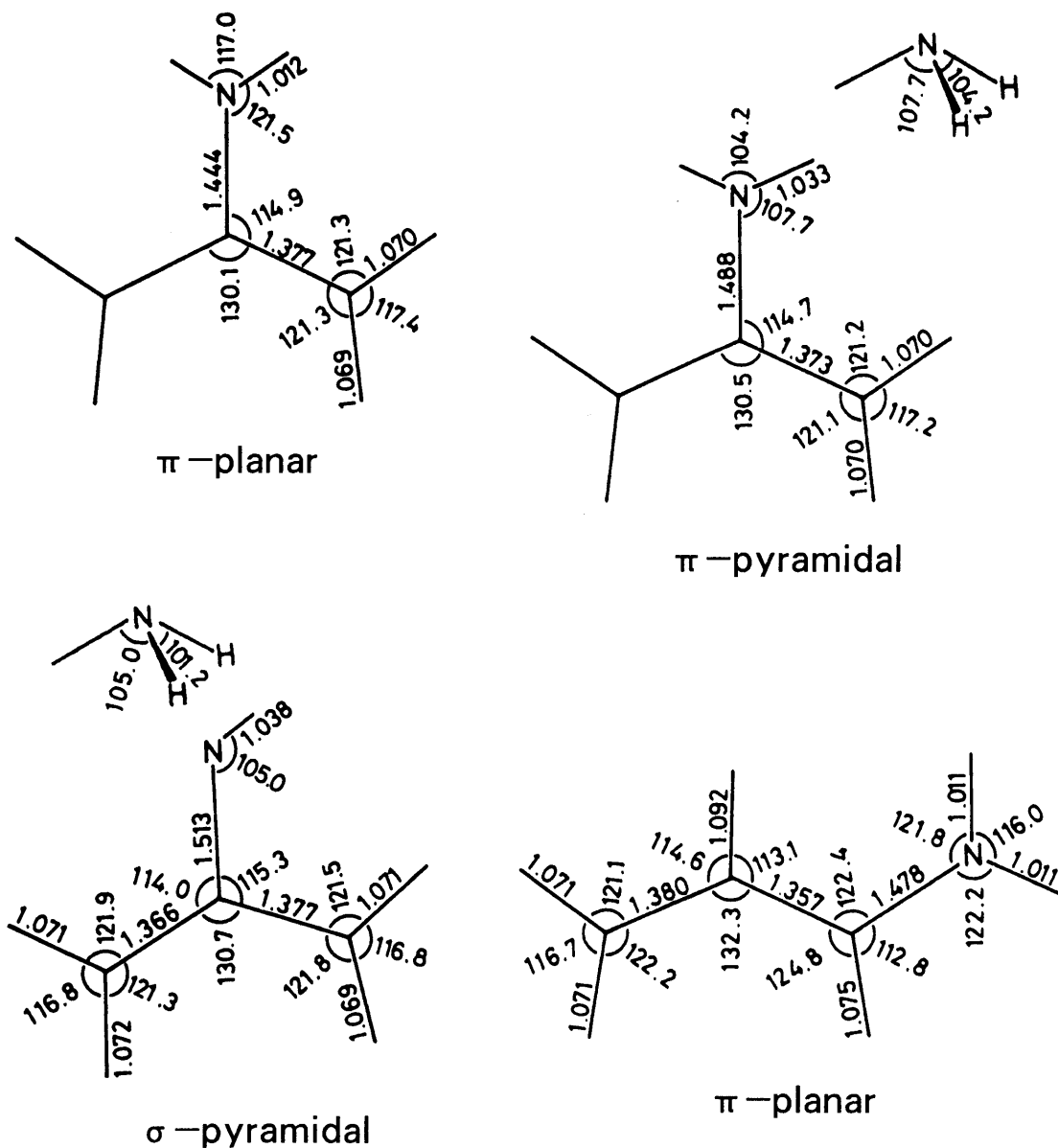


Figure 3. Optimized bond lengths in angstrom and bond angles in degree.

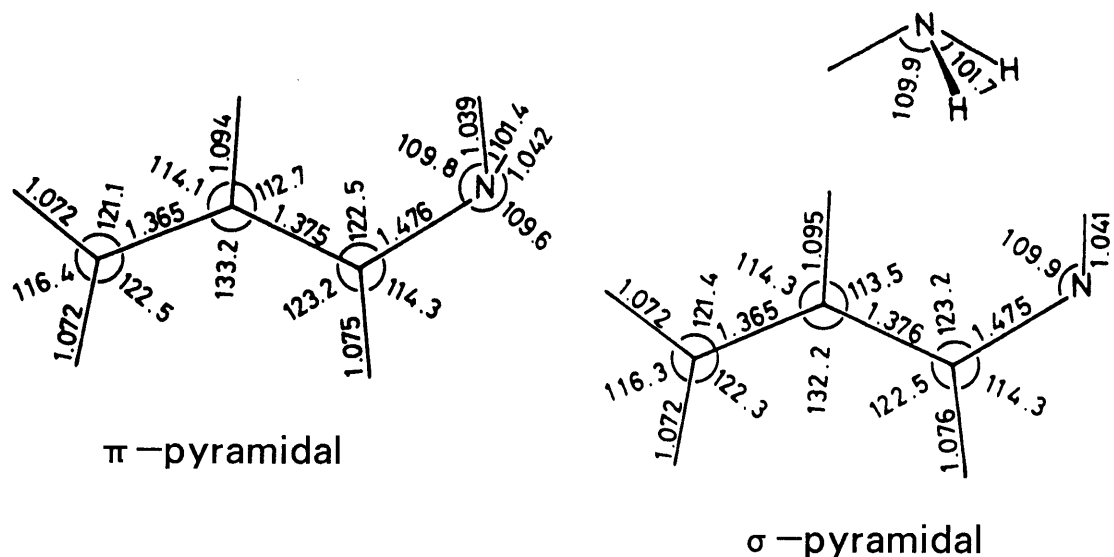
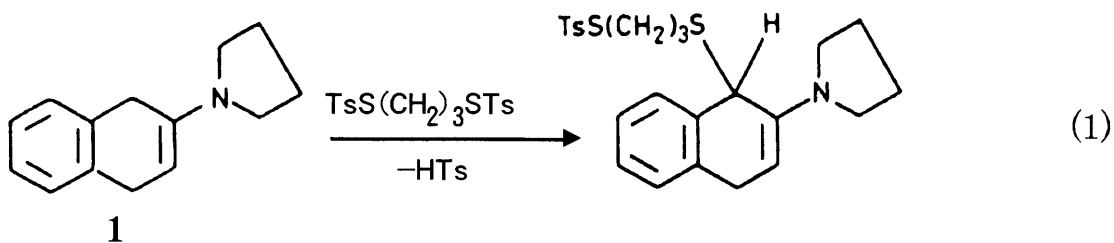
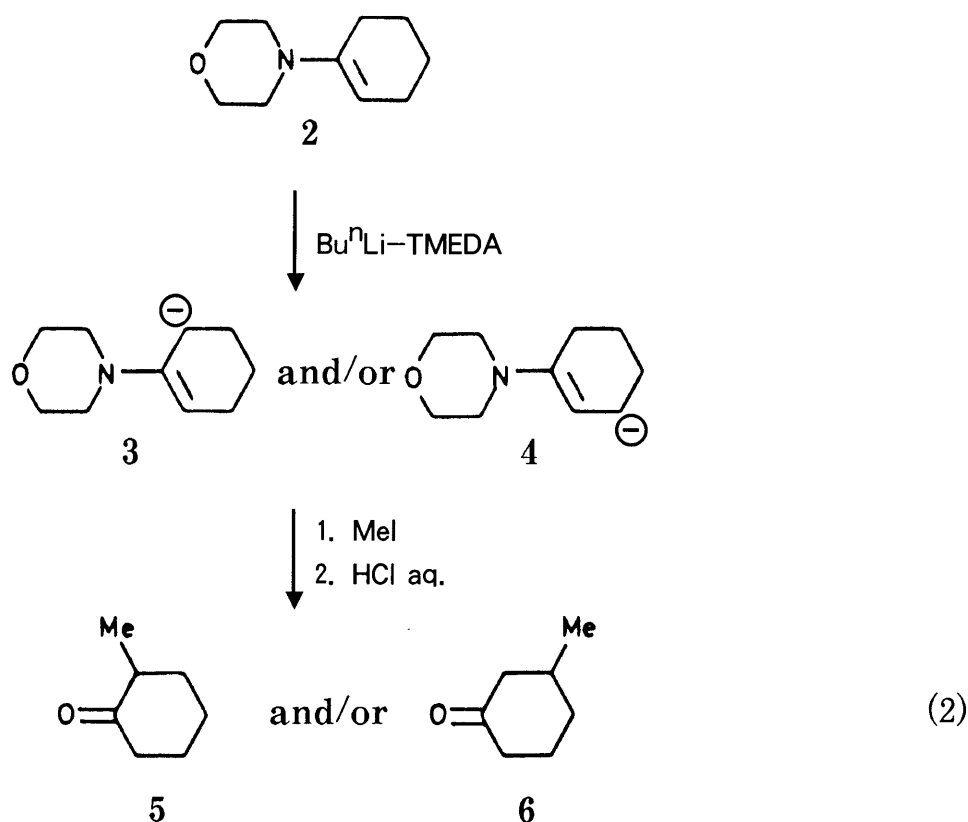


Figure 3. (Continued)

Experimental Confirmation. In order to test our prediction, enamines are required to have aliphatic substituents with abstractable hydrogens at both the α - and β -positions in chemically comparable environments. The number of experiments on these enamines reported so far is extremely limited. Woodward et al.³ showed that 2-pyrrolidino-1,4-dihydronaphthalene (**1**) undergoes deprotonation of the α -substituents (Equation 1). In our experiments less perturbed enamine, 1-morpholinocyclohex-1-ene (**2**), was used to confirm and generalize the theoretical prediction. The results of



deprotonation by $\text{Bu}^n\text{Li-TMEDA}$ followed by methyl iodide quenching (Equation 2) are listed in Table 2. No trace of 3-methylcyclohexanone was detected irrespective of the reaction time (1-72 h) and the molar ratio of $\text{Bu}^n\text{Li-TMEDA}$ to the substrate (1-20). The results strongly suggest that the 2-aminoallyl anion (3) is more stable than the 1-aminoallyl anion (4).



A similar orbital phase argument is applicable to the relative stabilities of 1- and 2-alkoxyallyl anions. Methyl cyclohexenyl ether was employed as a model compound. The results of deprotonation followed by methyl iodide quenching are listed in Table 2. The sole product is 2-methylcyclohexanone. The predicted stability of the 2-alkoxyallyl anion relative to the 1-isomer was found to be overwhelming.

Table 2. Yields of Methylcyclohexanones

substrate	equivalent of Bu ⁿ Li-TMEDA	reaction time (h)	yield (%)	
			5	6
1-morpholinocyclohex-1-ene	1	1.0	26	0
	1	2.0	35	0
	5	2.0	58	0
	10	2.0	64	0
	20	2.0	76	0
	3	1.0	45	0
	3	72	63	0
methyl cyclohexenyl ether	1	2.5	26	0
	2	2.0	58	0
	5	2.0	65	0

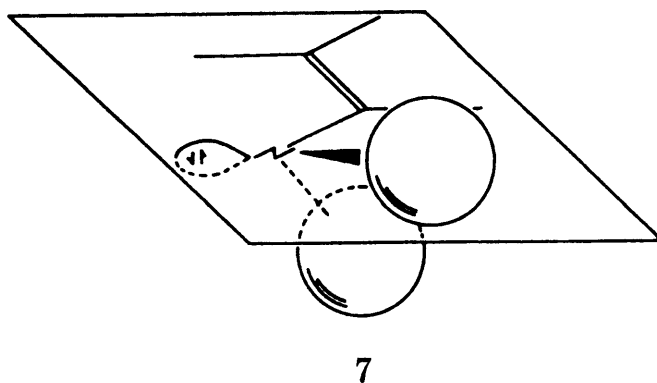
Discussion

The relative stability of allyl anion with 1- and 2-substituents that have a lone pair of electrons can be predicted by the frontier orbital interaction between the allyl anion moiety and the substituents. The LUMO of the allyl anion has greater extension at the central carbon. The HOMO of the substituent is the nonbonding orbital. The HOMO-LUMO interaction is then expected to lead to more stabilization in the 2- than the 1-substituted anions. It is interesting that the same conclusion can be drawn from the continuity-discontinuity of the orbital phase in noncyclic conjugation and from the frontier orbital amplitude. At present, the generality of the parallelism of both approaches remains open to question.

Recently, the trimethylenemethane dianion was observed⁴ to be thermodynamically more stable than butadiene dianion. The dianions are isoelectronic with 2- and 1-aminoallyl anions, respectively. The relative stability can be explained in a similar manner.²

As regards organic synthesis, these seems to be no superiority of the enamine anion routes for introducing substituents into ketones, as long as the lone pair of electrons on nitrogen is allowed to conjugate. The enamine routes lead to α -substituted ketones, and do not alter the regioselectivity of the reactions via enolate anion. The ab initio molecular orbital calculations of the σ -models are noteworthy in this respect. The STO-3G/STO-3G and 4-31G/STO-3G results

show an opposite thermodynamic preference of the isomeric aminoallyl anions. The relative stability deserves further investigation in more detail, since some enamines may undergo deprotonation from the γ -position to give 1-aminoallyl anions according to the STO-3G/STO-3G result. The process could provide a short route to β -substituted ketones. In other words, the enamine anions of the σ -models can serve as homo-enolate anion equivalents. The lone pair of electrons must be forced to lie on the σ -plane by some constraints for this purpose. A promising strategy is to attach bulky substituents to the heteroatoms to prevent the lone pair from π -conjugation (7).



Experimental

A mixture of 1-morpholinocyclohex-1-ene or methyl cyclohexenyl ether with an n-butyllithium-tetramethylethylenediamine complex ($\text{Bu}^n\text{Li-TMEDA}$) was stirred under an atmosphere of argon at room temperature, and was then

quenched by methyl iodide at -20°C . After hydrolysis with hydrochloric acid followed by extraction with ether the reaction mixture was subjected to g.l.c. analysis on dioctyl phthalate (DOP).

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Chapter 2

Orbital Phase Design of Noncyclic Electron Localizing and Delocalizing π -Conjugated Polyions and Related Systems

Abstract: Noncyclic localization–delocalization of electrons in π -conjugated hydrocarbon polyions was predicted in terms of the continuity–discontinuity of the phase of the component orbitals. Many pairs of electron–localizing and –delocalizing conjugated polyions were designed as the model systems of which the relative stabilities have not been explored so far.

The concept of localization and delocalization of electrons is fundamental in organic chemistry. Among the prominent examples are the $4n + 2 \pi$ electron rule for aromaticity¹ and the stereoselection rule for pericyclic reactions.² The frontier orbital theory for chemical reactivity³ emphasizes the delocalization between the molecules or bonds. The charge transfer force for intermolecular complexation of electron donor and acceptor⁴ belongs to this category. An

introduction of orbital symmetry or phase argument^{2,3} makes substantial progress in the theory of cyclic localization and delocalization. Chemical reactions via cyclic transition state are under control of the frontier orbital phase of the reacting molecules or parts of molecules or under the conservation of orbital symmetry.

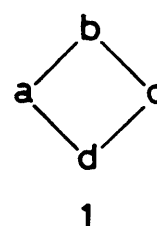
Recently, mechanism of cyclic delocalization among more than two molecules, molecular fragments, or bonds was examined to derive the orbital phase continuity conditions for cyclic delocalization:⁵ (a) the most electron-donating orbitals out of phase; (b) the most electron-accepting orbitals in phase; (c) the most electron-donating and -accepting orbitals in phase. The most electron-donating orbital is the HOMO of molecular systems, a bonding orbital of a bond, or a non-bonding orbital of lone pair electrons. The most electron-accepting orbital is the LUMO of molecular systems, an antibonding orbital of a bond, or a vacant orbital on cationic centers. Electron-delocalizing systems are here defined as those which meet the three orbital phase requirements simultaneously. Otherwise, conjugate systems are classified into electron-localizing ones. The orbital phase conditions were already shown^{5,6} to cover the aromaticity rule and the stereoselection rule.

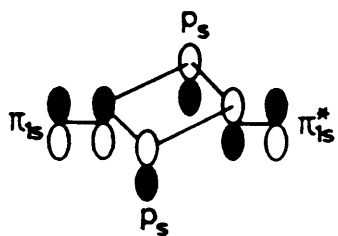
More recently, cyclic orbital interaction was shown to be contained in noncyclic conjugation.⁷ The orbital phase conditions for cyclic delocalization are also applicable to estimating the degree of noncyclic delocalization. Unfortunately, the related chemical phenomena observed so far are limited.

In this chapter we attempt to explore some new aspects of noncyclic conjugation in view of continuity and discontinuity of orbital phase. π -Conjugated hydrocarbon polyions are employed as the model species.

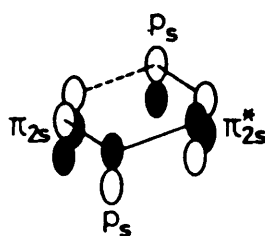
Orbital Phase Design

Suppose that four orbitals, a, b, c, and d, interact in a cyclic manner in which the orbital sequence is illustrated in 1. The interaction is hereafter denoted by the cyclic -a-b-c-d- interaction. The orbitals treated here are limited to occupied (p) and vacant (p^*) p-orbitals of ionic centers and bonding (π) and antibonding (π^*) orbitals of a π -bond. The π and π^* orbital can interact with the others at the same or different atomic orbital. The former one-centered interaction is denoted by the subscript, 1, the latter two-centered interaction by 2. The other subscripts, s (suprafacial) and a (antarafacial), are introduced to specify where an orbital takes part in cyclic interaction at the same or opposite side of orbital lobes. For a given set of orbitals, there are many possible modes of cyclic interactions which differ from one another in the orbital sequence, the interacting lobe (s or a) or center (1 or 2). Some interactions are those contained in real molecular systems, the others being not. The orbital interactions are subjected to the orbital phase analysis to

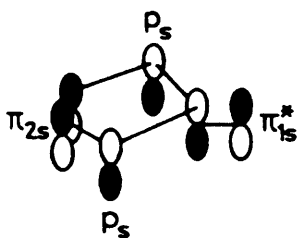




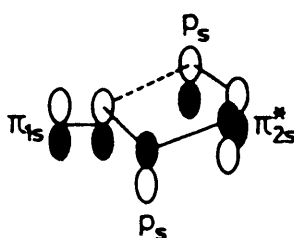
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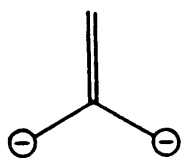
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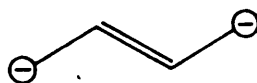
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5



6



7

predict that the associated molecular systems are electron-localizing or -delocalizing.

We start with cyclic $-\pi_s-p_s-\pi^*_s-p_s-$ interactions. The orbital sequence and the interacting lobes are given there. Whether the π and π^* orbitals interact at one or two centers makes a difference. There are four modes of interactions: $-\pi_{1s}-p_s-\pi^*_{1s}-p_s-$ (2), $-\pi_{2s}-p_s-\pi^*_{2s}-p_s-$ (3), $-\pi_{2s}-p_s-\pi^*_{1s}-p_s-$ (4), $-\pi_{1s}-p_s-\pi^*_{2s}-p_s-$ (5) interactions. When we apply the orbital phase condition, we can classify the cyclic orbital interactions into electron-localizing and -delocalizing ones.

The p and π orbitals are electron-donating, and the π^* orbital is an electron-accepting orbital.

In **2** all relations between the neighboring orbitals meet the phase requirements: the electron-donating π and p orbitals out of phase, the donating p and accepting π^* orbitals in phase. The interaction is electron-delocalizing. The conditions cannot simultaneously be satisfied in **3**, where the dotted line between the p_s and π_{2s} orbitals in phase indicates that the phase relation is opposite to the requirement. The interaction is electron-localizing. Similarly, the remaining interactions, **4** and **5**, are predicted to be delocalizing and localizing, respectively. The cyclic orbital interactions, **2** and **3**, are associated with real noncyclic conjugated species, as previously shown⁷ and will be briefly described in the following paragraph: the electron-delocalizing interaction **2** with trimethylenemethane (TMM) dianion (**6**) and the localizing interaction **3** with butadiene (BD) dianion (**7**). There are no actual noncyclic systems related to the remaining interactions (**4**, **5**).

Dianions of TMM and BD are considered to be composed of two anionic centers and a double bond. The electron delocalization among the three systems is described in terms of the configuration interactions or the orbital interactions as is schematically represented in Figure 1a.⁷ An electron shifts from a anionic center to the double bond through the interaction of the ground state configuration, G, with the electron-transferred configuration, T_1 . The configuration interaction is approximated to be the interaction of the p-orbital of the

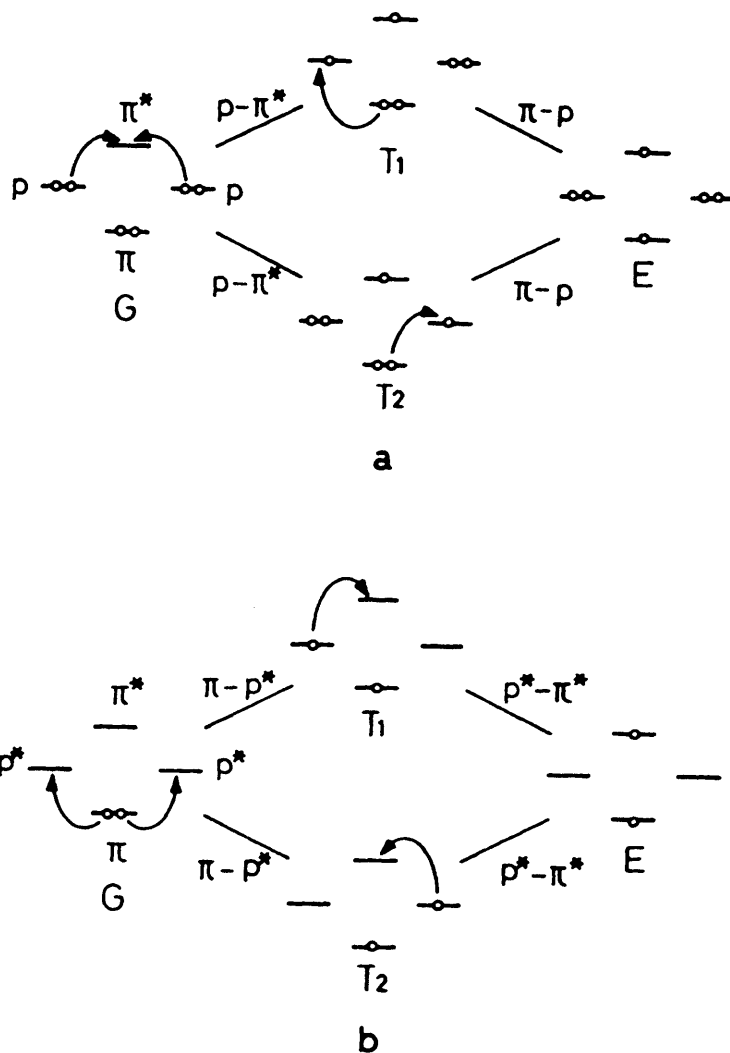
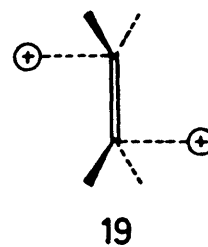
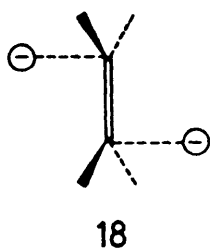
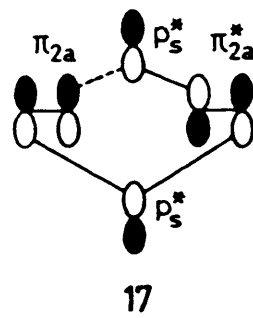
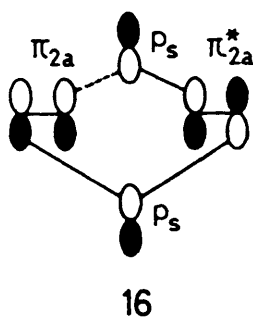
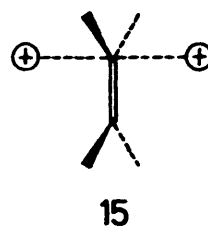
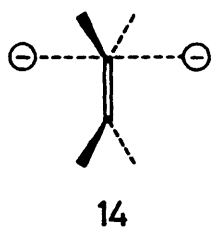
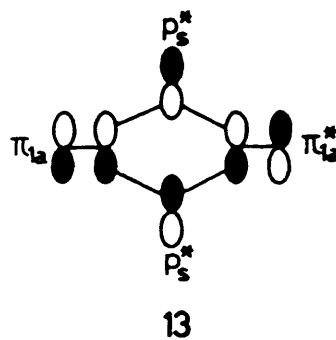
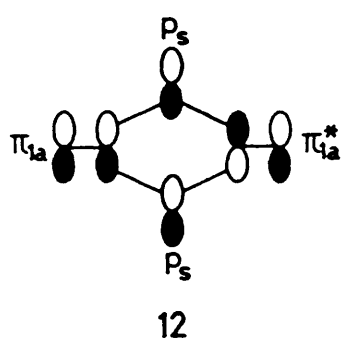


Figure 1.

anionic center with π^* orbital of the double bond. An electron hole results from the transfer. The hole can be supplied with an electron from double bond through the interaction of the transferred configuration with the locally-excited configuration, E. The T_1 -E configuration interaction corresponds to the $p-\pi$ orbital interaction. As a result, the G- T_1 -E configuration interaction or the $\pi-p-\pi^*$ orbital interaction is

involved in the above process. There is an analogous process starting with an electron shift from the other anionic lone pair orbital. The process involves the G-T₂-E configuration interaction or the π -p- π^* orbital interaction, where the p orbital is different from that in the aforementioned process. All interactions are suprafacial. Now we realize that the delocalization involves the cyclic $-\pi_s$ -p_s- π^*_s -p_s- interaction. In the TMM dianion both anionic centers interact with the same carbon of the double bond. The π and π^* orbitals take part in cyclic interaction at one center (π_{1s} , π^*_{1s}) as is shown in **2**. In the BD dianion the anionic centers interact with the different carbons of the double bond. The two-centered interaction at the π and π^* orbitals (π_{2s} and π^*_{2s}) are involved in cyclic interaction (**3**).

We have examined cyclic $-\pi_s$ -p_s- π^*_s -p_s- interactions which have been found to include the orbital interactions for the dianions of TMM and BD. We replace p_s by p^{*}_s to examine the corresponding dication. Similar arguments leads to a $-\pi_{1s}$ -p^{*}_s- π^*_{1s} -p^{*}_s- interaction (**8**) and a $-\pi_{2s}$ -p^{*}_s- π^*_{2s} -p^{*}_s- interaction (**9**) in place of **2** and **3**. The interactions are similarly associated with real systems; those corresponding to **4** and **5** being not. The interaction, **8**, is electron-delocalizing, while **9** is electron-localizing. The delocalizing interaction is contained in the TMM dication (**10**), the localizing one in the BD dication (**11**) as is shown in Figure 1b. An electron shifts from a double bond to a cationic center through the G-T₁ interaction. The configuration interaction

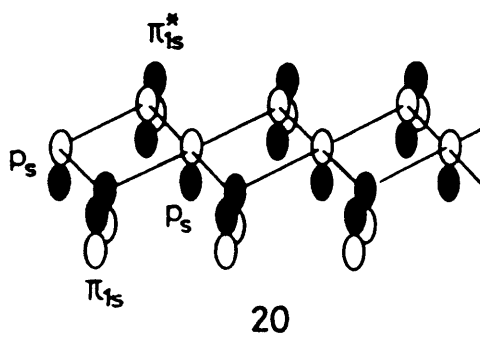


TMM dianion corresponds to the $-\pi_{1a}-p_s-\pi_{1a}^*-p_s-$ interaction (12). That (8) contained in TMM dication corresponds to the $-\pi_{1a}-p_s^*-\pi_{1a}^*-p_s^*-$ interaction (13). These are related to the antarafacial analogues of the TMM divalent ions,

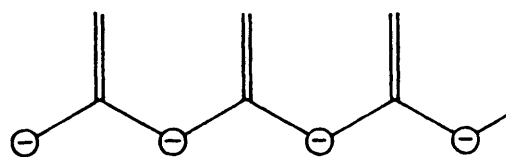
where a double bond interact with two ionic centers at the same carbon (14 and 15). Electron-localizing counterparts are the $-\pi_{2a}-p_s-\pi^*_{2a}-p_s-$ and $-\pi_{2a}-p_s^*-\pi^*_{2a}-p_s^*-$ interactions (16 and 17). The related systems are the antarafacial analogues of BD divalent ions (18 and 19).

We have described cyclic $-\pi-p^{(*)}-\pi^*-p^{(*)}-$ interactions and found that the orbital interactions (2, 3, 8, 9, 12, 13, 16, 17) are associated with the real molecular systems (6, 7, 10, 11, 14, 15, 18, 19), respectively. Although there are many other possible interactions of four orbitals, none of them are contained in real polyvalent ions. We will here design electron-localizing and -delocalizing species with more electronic charges by fusing the cyclic orbital interaction units for the divalent ions singled out above. Charge (positive or negative) does not alter the conclusion with respect to localization and delocalization,⁸ as can be seen in the preceding arguments. The following will be confined to polyions.

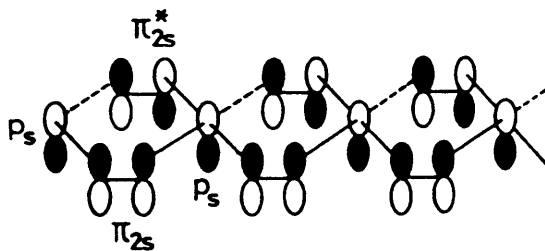
We first fuse the suprafacial interaction units, i. e., the delocalizing interaction, 2, and the localizing interaction, 3. The fusion of 2 at one of p_s 's gives rise to a delocalizing chain of cyclic orbital interaction (20). The related system is polyanion where each neighboring pair of TMM dianions share one of anionic centers (21). The localizing counterpart (22) similarly derives from 3. The cyclic orbital interaction corresponds to the polyanion (23) where anionic centers are shared by BD dianions. The two-site fused interactions (24 and 25) are those contained in the delocalizing dianion (26) and the localizing dianion (27).



20



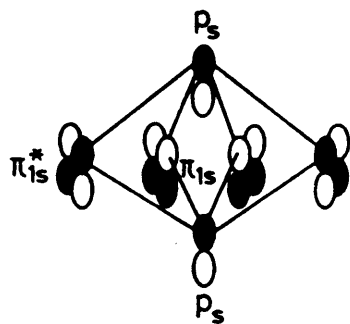
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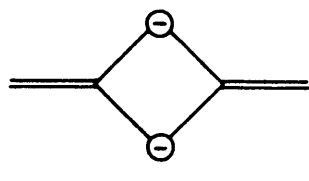
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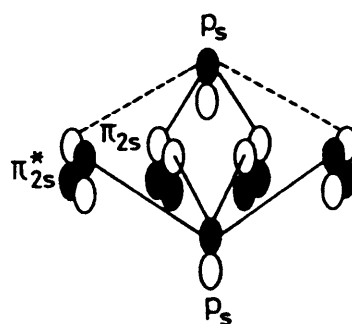
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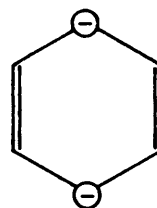
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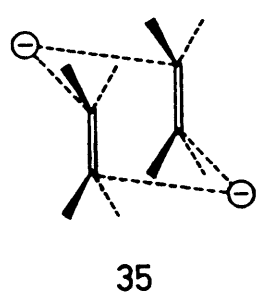
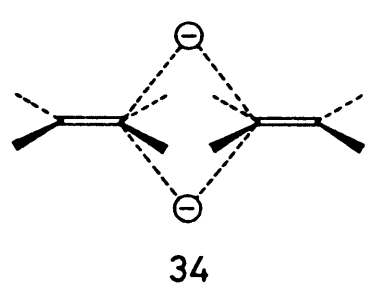
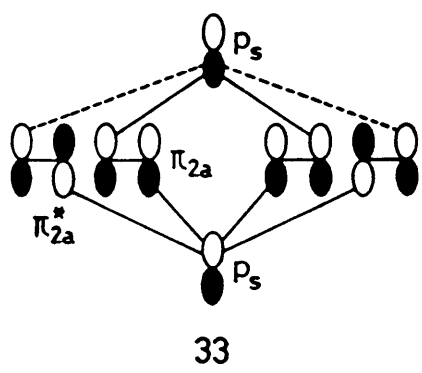
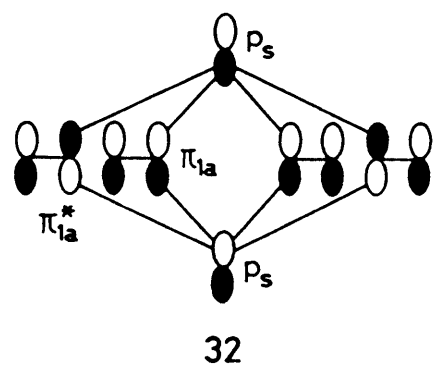
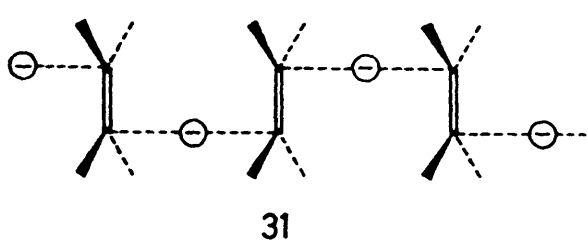
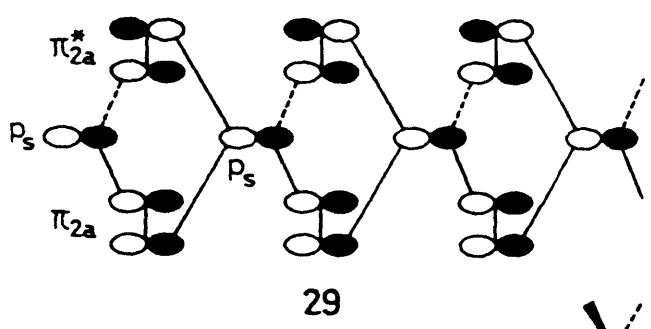
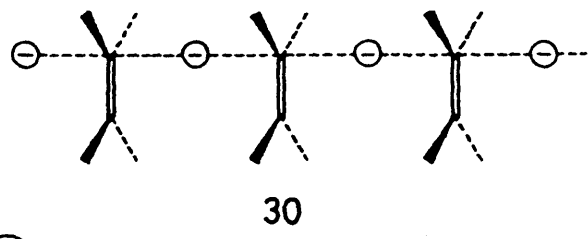
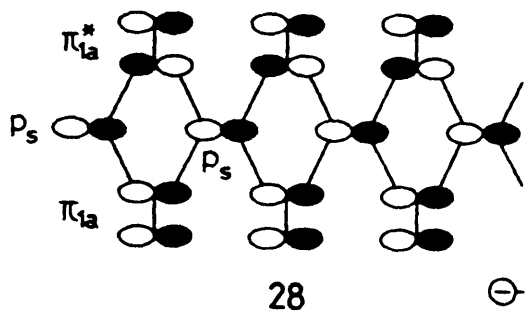
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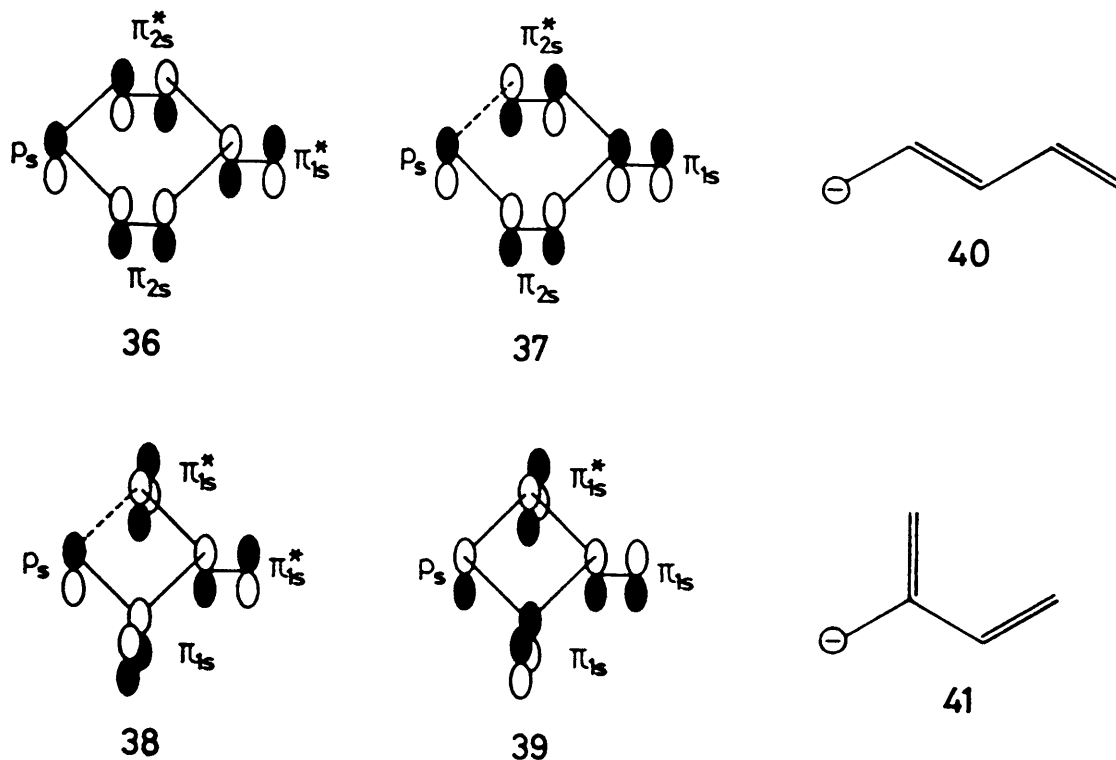
27



Secondly, we fuse the antarafacial interaction units, i. e., the delocalizing interaction (12) and the localizing interaction (16). Similar arguments lead to the delocalizing (28) and localizing (29) chains of cyclic orbital interactions in case of one-site fusion. These are associated to ions and double bonds stacked alternately (delocalizing 30 and localizing 31). The two-site fusion gives rise to the delocalizing (32) and localizing (33) arrays of orbitals, which are those contained in 34 and 35, respectively.

We have described the cyclic interactions of two $p^{(*)}$, π and π^* orbitals, which have been shown to be contained in the divalent ions of TMM and BD (6, 7, 10, 11) and their corresponding antarafacial analogues (14, 15, 18, 19) and designed electron-localizing and -delocalizing polyions (21, 23, 26, 27, 30, 31, 34, 35) by fusing them at one and two sites. We will next describe cyclic orbital interactions of one p orbital and three of π or π^* orbitals. The real noncyclic systems represented by some interactions, i. e., $-p-\pi^*-\pi^*-\pi-$ interactions (36, 38) and $-p-\pi^*-\pi-\pi-$ interactions (37 and 39), are monovalent ion units, i. e., the conjugated anions, 40 and 41, as will be shown in the following paragraph. We will then design some dianions by fusing the cyclic orbital interaction units in a different manner.

The mechanism of electron delocalization from the anionic center to the distant double bond through the middle bond in 40 and 41 is shown in Figure 2a. An electron shifts from the anionic center to the middle bond through the $G-T_1$ or $p-\pi^*$ interaction. The transferred electron shifts farther



to the terminal bond through the T₁-T₃ or π^{*}-π^{*} interaction. The process involves the p-π^{*}-π^{*} interaction. There is another path for the distant delocalization. An electron shifts from the middle to terminal bond through the G-T₂ or π-π^{*} interaction, leaving an electron hole in the middle π bond. The hole then shifts to the anionic center through the T₂-T₃ or p-π interaction. The process involves p-π-π^{*} interaction. As a result, the distant delocalization via the two paths contains the -p_s-π_s^{*}-π_s^{*}-π_s- interactions (36-39).

The cyclic interactions are identical with that involved in a way of polarization of the middle bond (Figure 2b). The electron shift from the anionic center to the middle bond leaves an electron hole which moves to the latter. The process involves the G-T₁-E or π_s-p_s-π_s^{*} interaction. In the

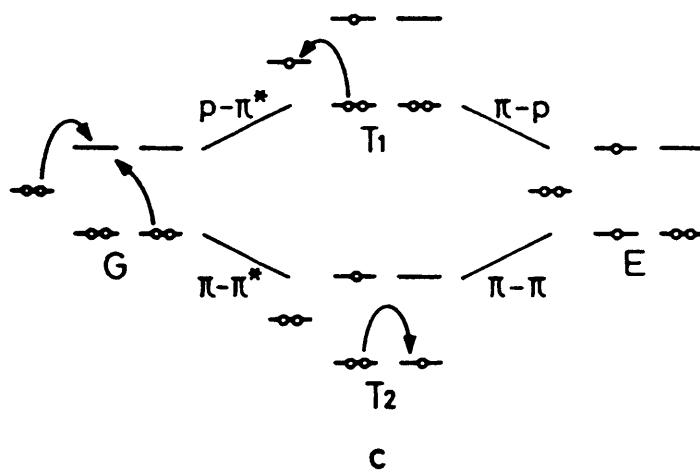
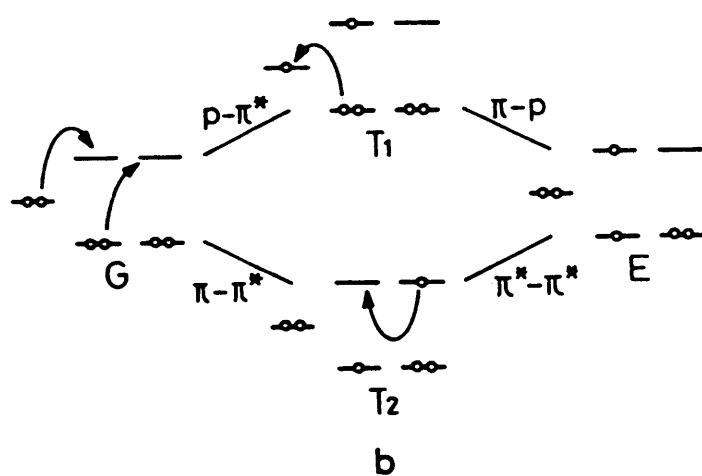
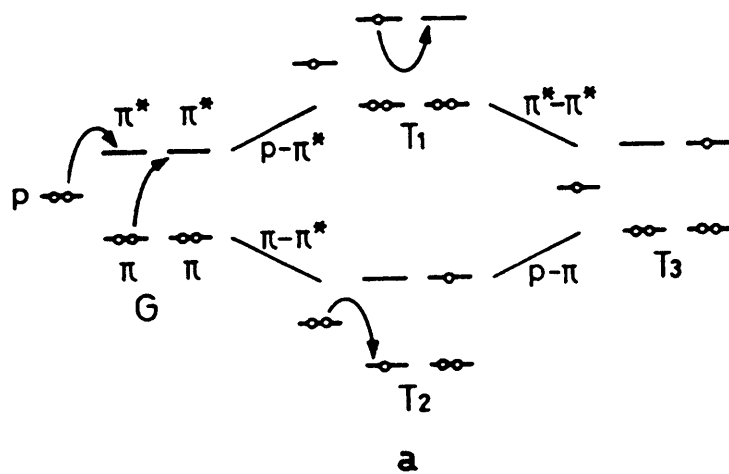


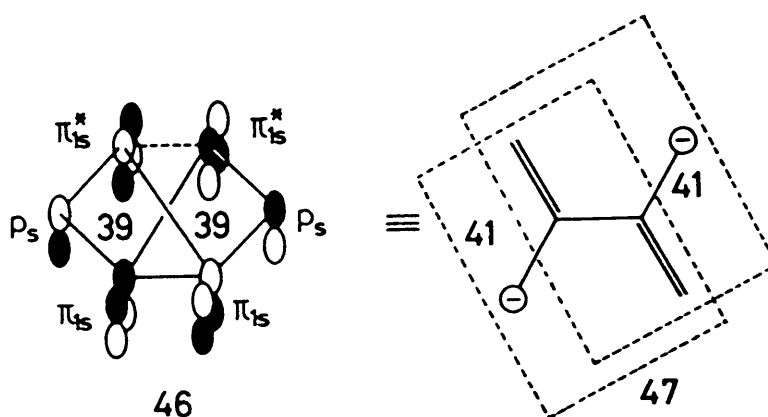
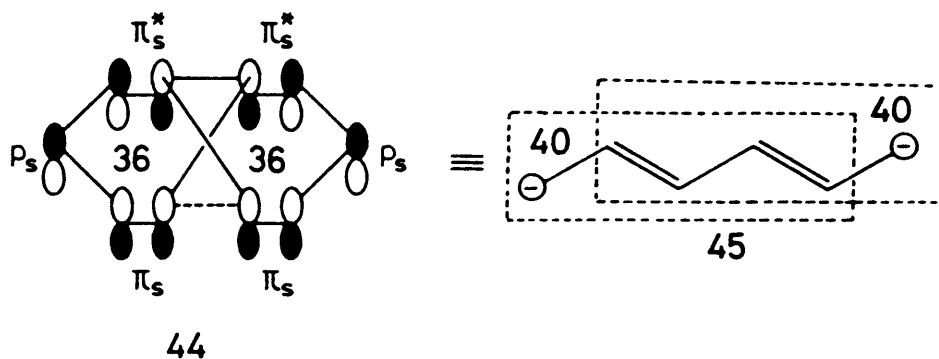
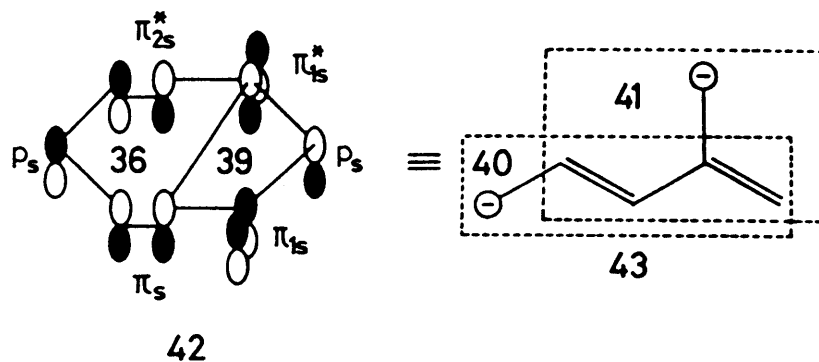
Figure 2.

other path, an electron first shifts from the middle to terminal bond and then back to the former through the G-T₂-E or $\pi_s - \pi_s^* - \pi_s^*$ interaction. As a result, the polarization involves the same $-p_s - \pi_s^* - \pi_s^* - \pi_s -$ interaction as the distant delocalization. The dual property of the cyclic orbital interaction should be noted for forthcoming arguments.

Another polarization path is shown in the bottom half of Figure 2c. The electron shift from the terminal to middle bond leaves an electron hole, which moves to the latter through the G-T₂-E or $\pi_s - \pi_s - \pi_s^*$ interaction. This forms a different cyclic $-p_s - \pi_s - \pi_s - \pi_s^*$ interaction with the $\pi_s - p_s - \pi_s^*$ interaction, which has been shown in the preceding paragraph to be involved in the polarization of the middle bond (The top halves of Figure 2b and 2c represent the identical process).

We have shown that cyclic orbital interactions of one p orbital and three π and π^* orbitals are contained in the conjugated monoanions. The cyclic orbital interaction with the dual nature – the distant delocalization of the lone pair electrons and the polarization of middle bond – is favored by phase continuity (36) in the anion 40, and disfavored by phase discontinuity (38) in the anion 41. The cyclic orbital interaction for the polarization only is favored by phase continuity (39) in 41, and disfavored by phase discontinuity (37) in 40.

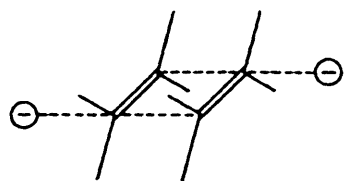
Now we design cyclic orbital interactions for dianions by fusing the delocalizing interaction units derived from the monoanions. The interaction (36) for the delocalization–



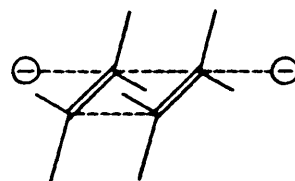
polarization in **40** and that (**39**) for the polarization in **41** are combined to share the neighboring pair of π_{2s} and π_{1s}^* in **36** and that of π_{1s} and π_{1s}^* in **39**. The resulting orbital interaction (**42**) is associated with the dianion (**43**) where the diene moieties in the monoanions are superimposed. When the orbital interactions (**36**) for the delocalization-polarization

are combined with each other to share the $\pi^*_{1s}-\pi^*_{2s}$ pairs, a cyclic interaction (44) for the dianion 45 is generated. A combination of the interactions (39) for the polarization to share the $\pi_{1s}-\pi_{1s}$ pairs leads to a cyclic interaction (46) for the dianion (47).

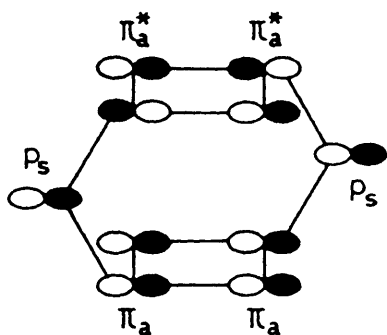
Now we predict the relative stabilities of the designed dianions. The cyclic orbital interaction unit (36) with the dual nature of delocalization and polarization should contribute to more stabilization than the polarization interaction (39). The stability is then expected to increase with the number of the delocalization–polarization interactions involved if there is no extra–stabilization on fusion. In the dianion 45 the cyclic orbital interaction units are both the delocalization–polarization interactions. The dianion 43 contains one, the remaining (47) none. The stability then decreases in the order of 45 > 43 > 47. However, the fusion of orbital interaction units can enhance the effects of each other as significantly as to invert the ordering. A pair of orbitals shared on fusion in 42 is a primary⁹ interaction between electron–donating and accepting orbitals. In addition, the cyclic six–orbital $-p-\pi^*-\pi^*-p-\pi-\pi-$ interaction in 42 satisfies the phase continuity requirements. In contrast, the orbital interactions shared in 44 and 46 are secondary⁹ between electron–donating orbitals or between electron–accepting orbitals. The extra–stabilization due to the fusion should be smaller, if any. In addition, the cyclic six–orbital $-p-\pi^*-\pi^*-p-\pi-\pi-$ interactions do not satisfy the phase continuity requirements.¹⁰ The extra stabilization on fusion is then expected to be greater in



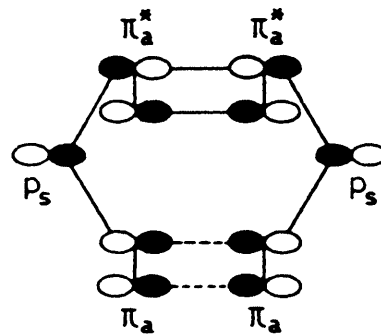
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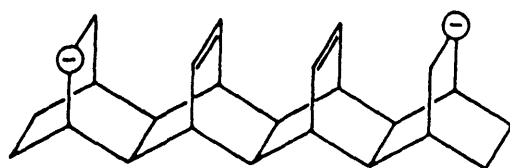
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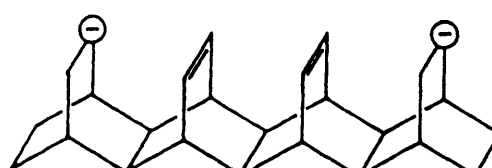
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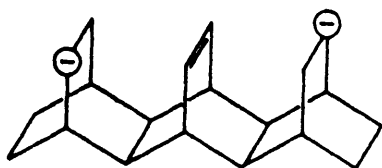
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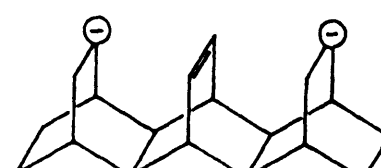
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54



55

43. The stability ordering of 43 and 45 might be inverted.

The conjugate dianions designed in the preceding sections are considered to be vinylogues of TMM and BD dianions. There is a pair of corresponding vinylogues of antarafacial analogues (14 and 18) of the TMM and BD dianions, where two juxtaposed π -bonds interact with two anionic centers in a different manner as shown in 48 and 49. The interactions

involved are cyclic six-orbital $-p_s-\pi_a^*-\pi_a^*-p_s-\pi_a-\pi_a-$ interactions, **50** and **51**. The cyclic six-orbital interaction is favored by the phase continuity (**50**) for **48** and disfavored by the phase discontinuity (**51**) for **49**. It follows that **48** is more stable than **49**. The relative stability makes a contrast with the aforementioned stability of the antarafacial analogues (**14**, **18**) of the TMM and BD dianions. We could experimentally examine the prediction by preparing such polycyclic species as **52–55**.

Geometry Optimization

The preceding orbital phase arguments have been limited to the localization–delocalization of π electrons, and have not taken into account the effects of σ electrons and inner-shell electrons. It is necessary to examine whether these effects may modify or alter the orbital phase predictions, and supplement the qualitative arguments by mean of numerical values. Molecular geometries of some ions are optimized by ab initio molecular orbital calculations with STO–3G basis set. The geometries fully optimized under given symmetry constraints are shown in Figure 3. The relative energies of the isomers to be compared are listed in Table 1.

The TMM dianion is estimated to be more stable by 22.5 kcal/mol than the BD dianion. The relative stability is consistent with the orbital phase prediction⁷ and with the experimental observation.¹¹ The bond lengths also support the

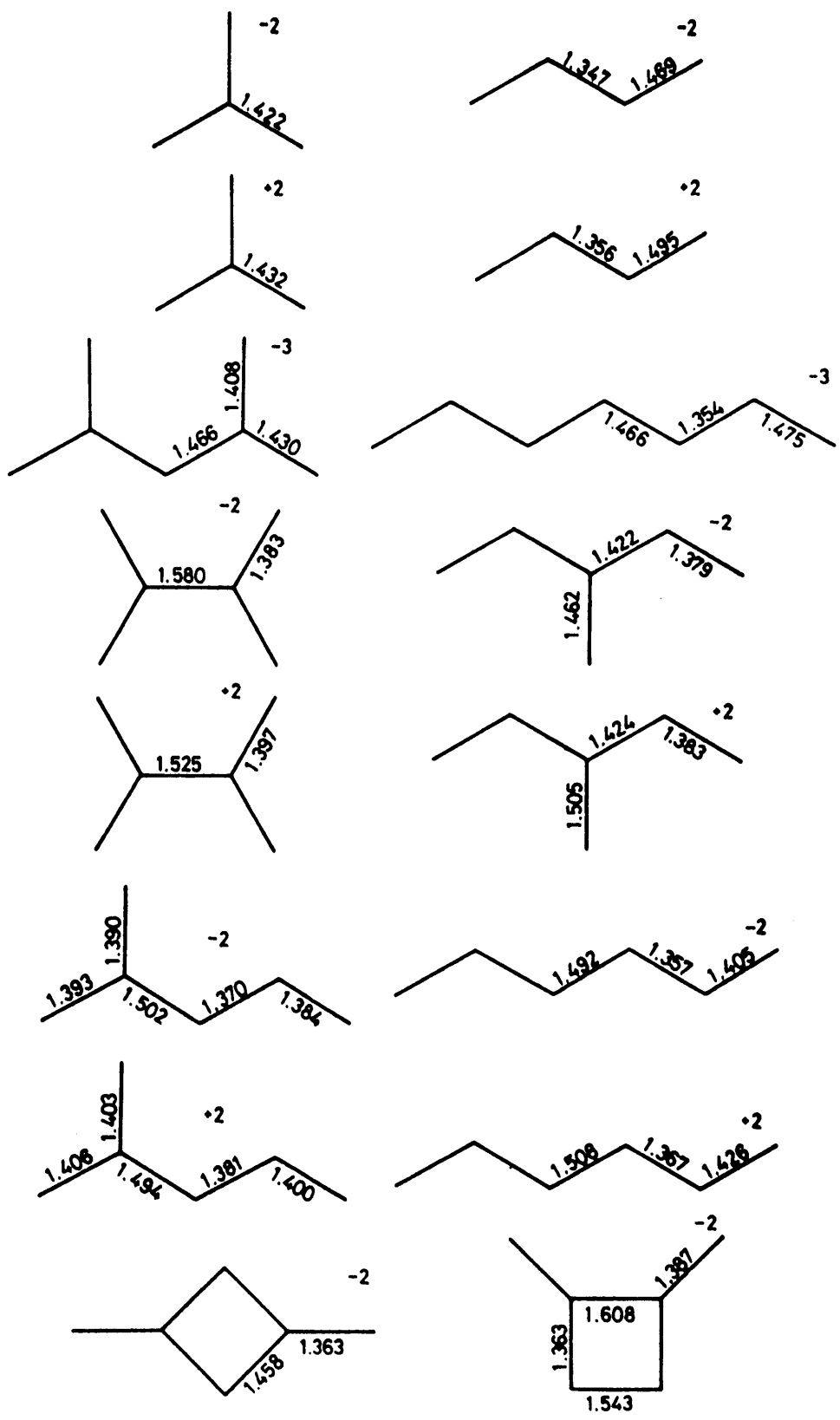


Figure 3.

preceding arguments. The bond alternation is remarkable in the electron-localizing BD dianion. The small distance (1.35 Å) between the inner carbons suggests a double bond character while the distance between the inner and outer carbon is long (1.47 Å). The carbon-carbon bond length (1.42 Å) in the electron-delocalizing TMM dianion is intermediate between those in the BD dianion.¹² Similar results are obtained for the TMM and BD dications. The energy difference is 18.1 kcal/mol. The bond lengths are 1.43 Å in the TMM dication, and 1.36 Å and 1.50 Å in the BD dication.

The one site fusion is found to still retain the delocalization and localization characters of the unit dianions. The fully cross conjugated C₇H₉ trianion¹³ (21) is more stable by 7.6 kcal/mol than the fully linearly conjugated C₇H₉ trianion¹⁴ (23). The bond alternation in the linear trianion is similar to that in the BD dianion. The short bond length is 1.35 Å, the long bond lengths being 1.47 Å and 1.48 Å. All the carbon-carbon bond lengths (1.41, 1.43, and 1.47 Å) in the cross trianion range between those in the linear trianion. Noteworthy is that the distance between the fused and central carbons in the TMM dianion unit is close to the larger distance in the linear trianion. The cross trianion tends to shift from the one-site fused pair of TMM dianions to two allyl anions connected with each other at their central carbons by an anionic carbon.

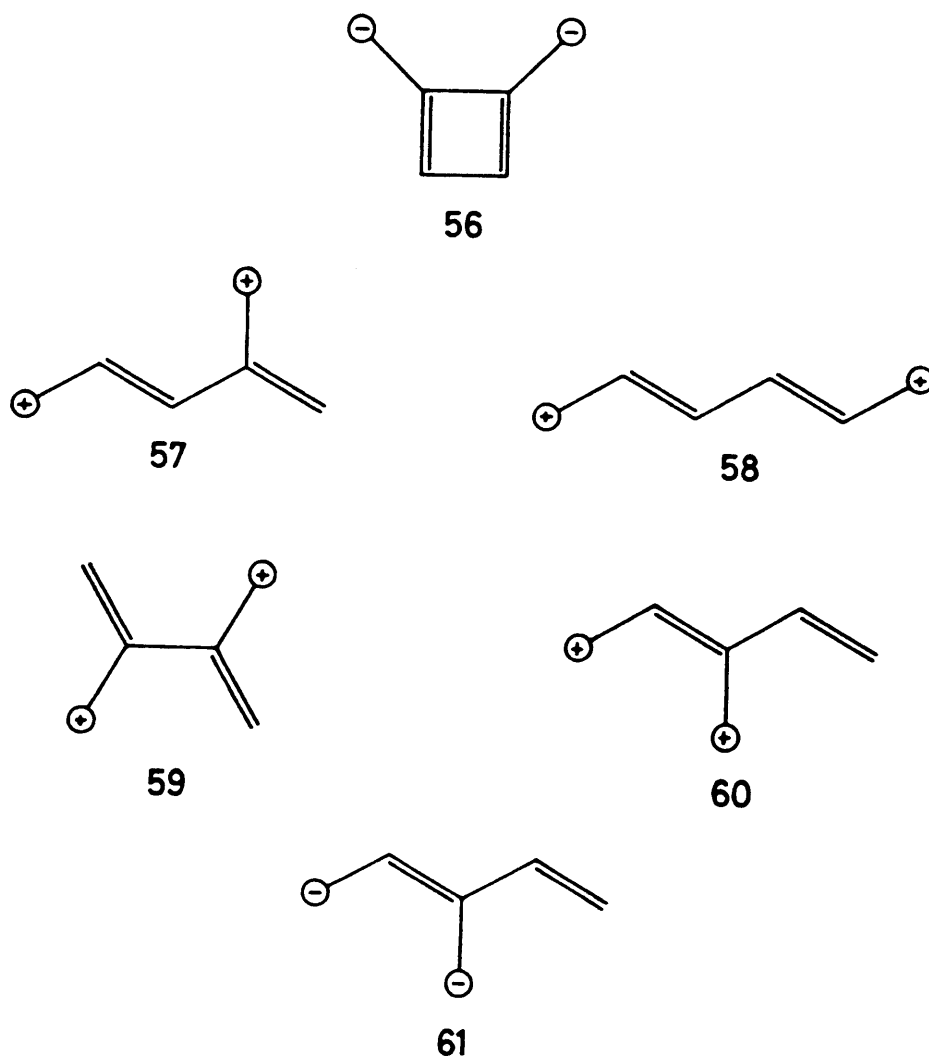
The two-site fusion of the TMM and BD dianion units gives rise to the four and six-membered ring dianions (26, 27). The direct comparison of the thermodynamic stabilities

Table 1. Relative Energies (kcal/mol) and Results of Configuration Analysis^a

molecule	geometry optimization		configuration analysis ^c			
	point group	relative energy ^b	GT	TE	TT	total
6	D _{3h}	0	+0.430	+0.139	–	+0.569
7	C _{2h}	+22.46	+0.286	0	–	+0.286
10	D _{3h}	0	+0.452	+0.144	–	+0.596
11	C _{2h}	+18.10	+0.257	0	–	+0.257
21 ^d	C _{2v}	0	+0.725	+0.208	+0.014	+0.947
23 ^d	C _{2v}	+7.62	+0.561	+0.001	+0.017	+0.579
26	D _{2h}	0	+0.606	+0.136	–	+0.742
56	C _{2v}	+29.21	+0.490	+0.070	+0.034	+0.594
43	C _s	0	+0.586	+0.108	+0.037	+0.731
45	C _{2h}	+1.24	+0.534	+0.042	+0.036	+0.612
47	D _{2h}	+17.27	+0.586	+0.111	+0.010	+0.707
61	C _{2v}	+53.40	+0.590	+0.039	+0.145	+0.774
57	C _s	0	+0.626	+0.113	+0.037	+0.776
58	C _{2h}	+1.31	+0.524	+0.043	+0.032	+0.598
59	D _{2h}	+12.64	+0.658	+0.011	+0.014	+0.683
60	C _{2v}	+53.31	+0.601	+0.046	+0.153	+0.800

^aWith STO–3G basis set. ^bThe reference is the total energy of the most stable isomer.

^cEach term is defined in the text (Equation 3). ^dTrianion.



due to π -electron delocalization is hampered by ring strain. The instability of benzene dianion is also a direct result of the Hückel rule. It is more interesting to compare the delocalizing dianion (**26**) with its four-membered ring isomer (**56**). The delocalizing **26** was estimated to be more stable by 29.2 kcal/mol. The bond lengths range less widely (1.36–1.46 Å). The structure of the 1,3-isomer deviates from formally fused TMM dianions toward a combined system of anionic centers and exocyclic double bonds. The 1,2-isomer tends to obtain a property of linearly-conjugated dianion by lengthening a bond in the ring.

Geometry optimization of C_6H_8 dications shows that the relative stability decreases in the order of **57** > **58** > **59**. The stability of **57** relative to **58** suggests the importance of the extra-stabilization by sharing the primary orbital interaction corresponding to **42** for the dianions. A conspicuous feature in the optimized geometry is a strong tendency toward two allyl cations. The linear dication appreciably alternates the single and double bonds. The remaining isomer of C_6H_8 dications, **60**, which has an electron-localizing BD dication unit, is the least stable. The geometry suggests that the dication is a combination of a pentadienyl cation and a cationic center. These results are almost the same as those of the dianionic analogues¹⁵ (**43**, **45**, **47**, **61**).

Electron Configuration Analysis for Many System Interaction

The ab initio calculations almost completely support the orbital phase predictions on the relative stabilities of the polyions, and give more detailed information of molecular geometries. Here we attempt to look into the relation of these calculated properties with the mechanism of electron delocalization among many bonds, cationic and anionic centers. We are concerned with the delocalization of π -electrons in conjugated polyions, composite systems of double bonds and anionic or cationic centers. The ground state configuration (G) has two electrons in each bonding orbital of double bonds and in each nonbonding orbital on the anionic

centers, and no electron in p-orbitals on the cationic centers. The delocalization is expressed by mixing the electron transferred configurations (T) and locally-excited configurations (E) into G. The ground state wave function is then formulated as

$$\Psi = C_G G + \sum_T C_T T + \sum_E C_E E + \dots \quad (1)$$

In the transferred configuration an electron is shifted from an occupied orbital of a bond or an anionic center to a vacant orbital of another bond or a cationic center. In the locally-excited configuration an electron is promoted from the bonding orbital to the antibonding orbital in a bond.

In general there are many Kekulé' structures for a given molecule. A Kekulé' structure corresponds to a ground state configuration. It is meaningful to analyze how electrons delocalize starting from the main Kekulé' structure. The electron configuration analysis for many system interaction (ECAMSI)¹⁶ is employed to single out the main Kekulé' structure. The wave function is subjected to ECAMSI for different ground state configurations or Kekulé' structures. The calculations yield the coefficients of G, T, and E configurations. The main Kekulé' structure is one with the biggest C_G .

Some quantities are defined to examine the delocalization in a qualitative manner. The integration of the normalized wave function (Equation 1) all over the space leads to the following equation:

$$\begin{aligned}
1 = & C_G^2 + \sum_T C_T^2 + \sum_E C_E^2 + \sum_T 2C_G C_T S(G, T) \\
& + \sum_{T_1 > T_2} 2C_{T_1} C_{T_2} S(T_1, T_2) + \sum_{T, E} 2C_T C_E S(T, E) + \dots \quad (2)
\end{aligned}$$

The square terms are the weights of electron configurations. The first cross terms represent the contribution from the G-T configuration interactions. This can be used as a measure of adjacent delocalization through the neighboring occupied and unoccupied orbital interactions. The second cross terms represent the contribution from the T-T configuration interactions. This can be used as a measure of distant delocalization beyond more than one systems through the interactions between the neighboring occupied orbitals and between the neighboring vacant orbitals. The third cross terms represent the contribution from the T-E configuration interactions. This can be used as a measure of polarization of bonds. The coefficients of configurations show the extent of contribution of each configuration to the electronic structure of a molecule. It has been shown that the ratios of coefficients of various configurations to that of the ground state configuration (C/C_G) are more preferable for comparing electronic structures of different molecules.^{7b} We discuss the results of configuration analysis on the basis of the coefficient ratios. The GT, TT, and TE terms of interest are defined as follows:

$$\begin{aligned}
GT &= \sum_T 2C_G C_T S(G, T) \\
TT &= \sum_{T_1 > T_2} 2C_{T_1} C_{T_2} S(T_1, T_2) \\
TE &= \sum_{T, E} 2C_T C_E S(T, E) \tag{3}
\end{aligned}$$

The main Kekulé structures are confirmed to be such forms as drawn. The results of configuration analysis on the optimized geometries are listed in Table 1. The relative stabilities are completely paralleled with the sums of three terms for the dianions of TMM and BD and for the one-site fused trianions. A difference in the electronic structures comes from the double bond polarizations. There is no double bond polarization ($C_E = 0.0$ therefore $T_E = 0.0$) in the electron localizing isomers (**7**, **11**, **23**), as has been predicted by the phase discontinuity of the cyclic orbital interaction. In the delocalizing ones the polarization contributes as significantly as the adjacent delocalization. According to perturbation theory the adjacent delocalization should be similar for the localizing and delocalizing pairs. The increment of the GT terms in the delocalizing isomers is considered to be induced by the allowed polarization.

The GT and TE terms of the delocalizing two-site fused dianion (**26**) are greater than those of the reference species (**56**), as was predicted. The relative stability can be similarly understood to be also due to the allowed bond polarization and the induced increment of the adjacent delocalization.

The most stable C_6H_8 dianion (**43**) has a greater sum of the three terms than the second (**45**). The magnitude of the GT term in **43** is due to the enhanced mixing of the transferred configuration or primary interaction between the $\pi-\pi^*$ interaction shared by the fused cyclic orbital interactions as has been described (**42**). The configuration coefficient ratio (0.24) of the transferred configuration is larger than that (0.17) of the corresponding transferred configuration in **45**. A similarly expected difference in polarization is found in the coefficient ratios. The ratio (0.32) of the locally-excited configuration for the cross-conjugated double bond in **43** is more than twice greater than that (0.13) in **45**.

There is a limit to the parallelism between the simply predicted or calculated stabilities and the results of configuration analysis. The sum of the three terms for the dianions (**47** and **61**) of lower stabilities are greater than that of more stable **43** or **45**. A possible explanation for the lost parallelism might be related with the "multiplicity" of the main Kekulé structure. The main Kekulé structure is uniquely determined "singlet" for **43** and **45** for which the sum of the three terms of configuration analysis is well correlated to the total energy. There is one more equivalent Kekulé structure for **47** and **61**, which are then expressed by the "doublet" Kekulé structures. The multiplicity arises from the discrepancy in symmetry between Kekulé structures and molecular geometries. Lower symmetry of Kekulé structures might enforce "undesirable" electronic rearrangements to recover the symmetry of electronic structures imposed by molecular ge-

ometries. The artificial failure inevitable results in overestimation of GT, TT, and TE terms.

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8. (a) The pioneering works by Clark, Schleyer and their collaborators have been encountered with greater difficulties in preparing dications^b than dianions^c of TMM, and they have been tempted to throw doubt on the thermodynamic stability of the dications. The TMM dianion with a phenyl group on each methylene was readily prepared at 20°C, whereas a reasonable synthetic route to the cor-

responding triphenyl TMM dication lead only to ring closure or intramolecular Friedel–Crafts reaction involving the aromatic moiety. This contrast may be attributable to the kinetic cause: Electrophilic aromatic substitutions are familiar while the substrates of nucleophilic ones are limited. The difficulties have been demonstrated by other attempts, but the origins seem unclear. There may be no well-established grounds for claiming that polycations and polyanions have similar stabilities. The similarities, which allow us to exclude a group of counterparts (polycations) from the arguments in the text, are the relative stabilities of isomeric ions. Meaningful is the comparison of the TMM dication with the BD dication, but not that of the dication with the dianion; (b) Schötz, K.; Clark, T.; Schleyer, P. v. R. *J. Org. Chem.* **1984**, *49*, 733. (c) Wilhelm, D.; Clark, T.; Schleyer, P. v. R.; Buckl, K.; Boche, G. *Chem. Ber.* **1983**, *116*, 1669.

9. According to the perturbation theory, the interaction between electron-donating and accepting orbitals is contained in the second-order energy terms, whereas those between donating orbitals and between accepting orbitals are contained in higher-order terms.⁵
10. On fusion there appears another cyclic six-orbital interaction, i. e., $-p-\pi^*-\pi-p-\pi^*-\pi-$ interaction. The orbital phase is continuous. However, the continuity does not promote electron delocalization because the donating and accepting orbitals are excessively alternated along the chain in the orbital cycle. For more details, see the con-

tinuity and discontinuity of cyclic conjugation.⁶

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12. (a) Some molecular orbital calculations of more realistic models with coordinated Li atoms have been reported. In the BD "dianion" lithium cations were indicated to bridge the terminal carbons symmetrically and doubly.^b The most stable structure of TMM "dianion" has a 1,3- and 1,3'-bridged structure (C_2),^c which was, however, found to be different from the X-ray structure of tribenzylidene-methane di(lithium tetramethylethylenediamine (TMEDA))^c: One lithium bridges the 1,3-positions of a allyl system while the other bridges the remaining carbons in 1,2-manner. The models for this structure (C_s) and with the highest symmetry (D_{3h}) were calculated to be higher in energy by about 4 kcal/mol. Anyway, we think that our dianion model is sufficient to compare the relative stabilities of polymetallated hydrocarbon isomers of the same number of carbons and charges but topologically different carbon skeletons. (b) Schleyer, P. v. R. *Pure Appl. Chem.* **1983**, *55*, 355. (c) Wilhelm, D. ; Dietrich, H. ; Clark, T. ; Mahdi, W. A. ; Kos, A. J. ; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1984**, *106*, 7279.
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Chapter 3

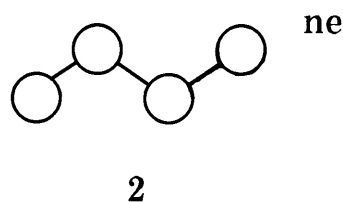
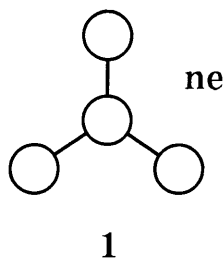
Cross vs. Linear Conjugation of Four p-Orbitals. Substituted Vinylcarbenes and Biscarbenes as Four π Electron Systems

Abstract: The application of the concept of cyclic orbital interaction in noncyclic conjugation developed recently has completed the relation between the stability of the cross vs. linear closed-shell conjugated systems of four p-orbitals and the number of electrons through the orbital-phase continuity-discontinuity properties. The cross conjugation is thermodynamically preferable in the case of $4n+2\pi$ electrons. The linear conjugation is preferable in the case of $4n\pi$ electrons. The fundamental features of some substituted vinylcarbenes and conjugated biscarbenes as model compounds for the four-electron system, disclosed by the ab initio molecular orbital calculations at the Hartree-Fock level, have been shown to be consistent with the qualitative theory.

Table 1. Orbital Phase Property

conjugation	cross	linear
2e/4p	continuous	discontinuous
4e/4p	discontinuous	continuous
6e/4p	continuous	discontinuous

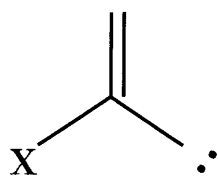
Recently, we showed that cyclic orbital interaction is involved in noncyclic conjugation.¹ According to the new insight the electron delocalization in noncyclic conjugated systems is under the control of the orbital phase as the delocalization in cyclic conjugated systems. Among the successful applications¹⁻³ is included a novel interpretation of the Y-delocalization introduced by Gund⁴ to explain the unique properties of guanidine and related chemical species. Six electrons can delocalize in four p-orbitals of cross conjugated systems (**1**, $n = 6$) since the phase of the orbitals involved is continuous (Table 1).¹ The potential significance of the 6e/4p conjugation was first noted by Finnegan⁵ for trimethylene-methane dianion (TMM²⁻), which was characterized by Klein and Medlik.⁶ A more recent advancement in the chemistry of TMM²⁻ and its derivatives appeared in some papers⁷ and was reviewed in some articles.⁸



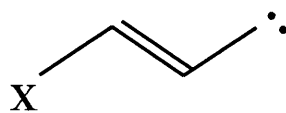
Interestingly as well, the concept of cyclic orbital interaction in noncyclic conjugation has revealed that the counterpart of the electron-delocalizing $6e/4p$ cross conjugation is the linear conjugation.¹ The linear $6e/4p$ conjugation (**2**, $n = 6$), of which the prototype is butadiene dianion (BD^{2-}),⁹ is electron localizing due to the orbital phase discontinuity. The theoretical prediction of the relative stability of the $6e/4p$ systems has been confirmed by experimental observation.¹⁰ Molecular orbital calculations have supported the relative stability. The Hess-Schaad resonance energy per atom has shown that TMM^{2-} is aromatic ($REPA = 0.069 \beta$) while BD^{2-} is antiaromatic ($REPA = -0.040 \beta$).¹¹ The ab initio molecular orbital optimization of geometry produced the remarkable energy difference (22.5 kcal/mol at STO-3G² and 26.4 kcal/mol at 6-31G¹²).

For the $2e/4p$ systems, the cross conjugation (**1**, $n = 2$) has been shown by the orbital phase property² to be thermodynamically preferable to the linear conjugation (**2**, $n = 2$). The ab initio molecular orbital calculation at the STO-3G level confirmed the prediction. The TMM dication is by 18.1 kcal/mol more stable than the BD dication.² Unfortunately, the chemistry of carbopolycations¹³ has been less advanced relative to that of carbopolyanions. The attempt to prepare a TMM^{2+} derivatives was not made until very recently. The first attempt was found to be hampered by undesirable intramolecular reactions.¹⁴

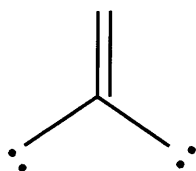
The relative stability of the cross-conjugated systems containing two and six electrons reminds us of the Hückel



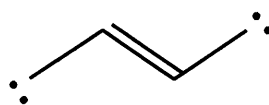
3



4



5



6

rule.¹⁵ The cross conjugation of four p-orbitals can be compared to monocyclic conjugation. Both prefer $4n+2$ electrons. If a similar analogy holds, the counterpart to the cross conjugation, that is, the linear conjugation of four p-orbitals could be compared to the Möbius conjugation.¹⁶ Both are relatively unstable with $4n+2$ electrons, as described above. Now we are interested in the $4e/4p$ systems. If the Hückel-Möbius analogy holds, the linear conjugation is thermodynamically favorable. A special example or the unequivocal stability of butadiene relative to trimethylenemethane diradical encourages our expectation. However, the generality remains to be explored. In this paper we compare the cross with linear $4e/4p$ conjugated systems other than butadiene and trimethylenemethane diradical.

Some vinylcarbenes (3, 4) with lone pair electrons on the substituent X ($X = \text{CH}_2^-, \text{NH}_2, \text{OH}, \text{SH}$) were employed as model compounds. The cross-conjugated systems (3) have

the substituents at the central carbon of the vinylcarbene and the linear ones (4) at the terminal olefinic carbons. Both substituent and the double bond provide the conjugation with two electrons. The vinylcarbenes are 4e/4p systems if the vacant p-orbital on the carbene center takes part in the conjugation. This is the case with the planar conformers. We used this model in order to compare the cross with the linear 4e/4p conjugation. If the lone pair electrons on the carbene center is in conjugation, the vinylcarbenes are 6e/4p systems. This is the case with the vertical conformers where the bond between the hydrogen atom and the carbene center is bent out of plane. The model compounds allowed us to compare the cross with linear 6e/4p conjugations. The comparison of the planar with the vertical conformers enables us to examine the relative stability of the 4e/4p and 6e/4p systems.

Another pair of cross and linear model compounds are conjugated biscarbenes (5, 6). These species can be 2e/4p, 4e/4p, or 6e/4p. Planar structures are expected to provide the conjugation with vacant p-orbitals on the carbene centers. These serve as 2e/4p models. With one bond between the carbene center and the hydrogen atom bent out of plane, the biscarbene can be 4e/4p models due to the additional two electrons in the nonbonding orbital on the carbene centers. With two out of plane C-H bonds, the species serve as the 6e/4p models.

The vinylcarbenes have been postulated as reaction intermediates so far.¹⁷ Some theoretical studies have been made at a variety of sophistication.¹⁸ However, neither experimen-

tal nor theoretical evidence is now available for chemical difference between the cross- and linear-substituted vinylcarbenes. On the other hand, the conjugated biscarbenes have been rarely documented except the aromatic polycarbenes¹⁹ which are considered as model compounds for organic ferromagnets.

Mechanism of Electron Delocalization in the 4e/4p Systems

We describe the mechanism of electron delocalization, the cyclic orbital interaction involved, and the orbital phase property. The model 4e/4p systems are considered to be composed of three subsystems (Figure 1). A double bond with two electrons interacts with a lone pair of electrons on the substituent X and with a vacant p-orbital on the carbene center. The occupied bonding and vacant antibonding orbitals are denoted by π and π^* ; the occupied nonbonding orbital by n, and the vacant p-orbital by p^* .

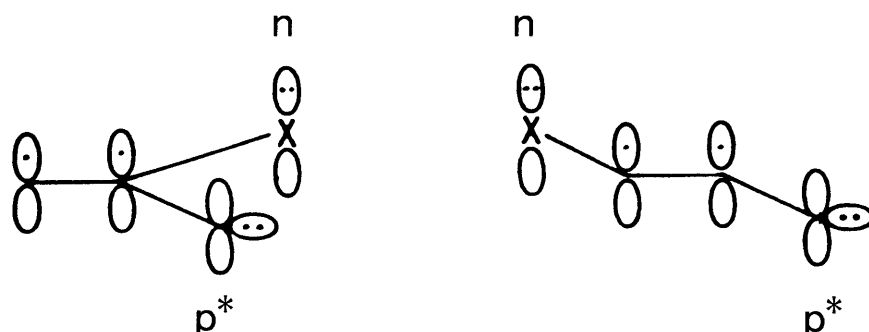


Figure 1. Cross and linear conjugations in substituted vinylcarbenes.

The mechanism of the delocalization from n to p^* via the double bond is schematically represented in Figure 2a. An electron shifts from n to π^* through the interaction of ground state configuration, G , and the transferred configuration, T_1 . The $G-T_1$ interaction is approximated to the $n-\pi^*$ interaction. The electron shifts farther to p^* through the T_1-T_3 or π^*-p^* interaction. The sequential $G-T_1-T_3$ or $n-\pi^*-p^*$ interaction is involved in this process. There is another delocalization process. An electron shifts from π to p^* through the $G-T_2$ or $\pi-p^*$ interaction. The resulting electron hole in the π orbital is supplied with an electron from n through the T_2-T_3 or $n-\pi$ interaction. The $G-T_2-T_3$ or $n-\pi-p^*$ interaction is involved in the delocalization process. As a result, the above two processes form the cyclic $-G-T_1-T_3-T_2-$ or $-\pi-p^*-\pi^*-n-$ interaction.

The mechanism of polarization of the double bond is similarly shown in Figure 2b. An electron shifts from n to π^* through the interaction of the $G-T_1$ or $n-\pi^*$ interaction, leaving an electron hole. The hole is supplied with an electron from π through the interaction of T_1 with the locally-excited configuration, E , or through the $n-\pi$ interaction. The $G-T_1-E$ or $\pi-n-\pi^*$ interaction is involved in the polarization process. There is another way of polarization. An electron shifts from π to p^* through the $G-T_2$ or $\pi-p^*$ interaction. The electron shifts back to π^* through the T_2-E or $p^*-\pi^*$ interaction. The $G-T_2-E$ or $\pi-p^*-\pi^*$ interaction is involved in this process. The two polarization processes form

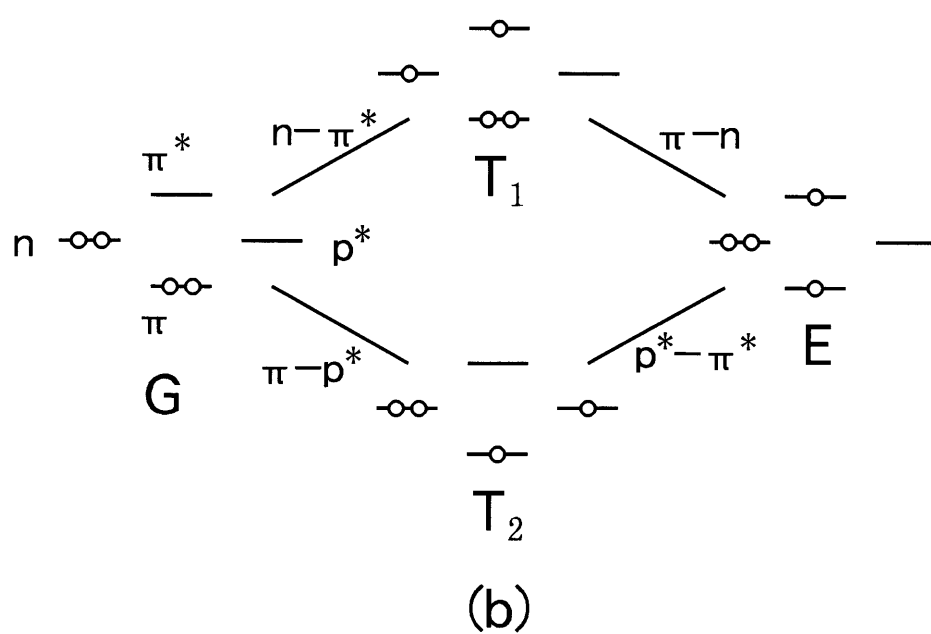
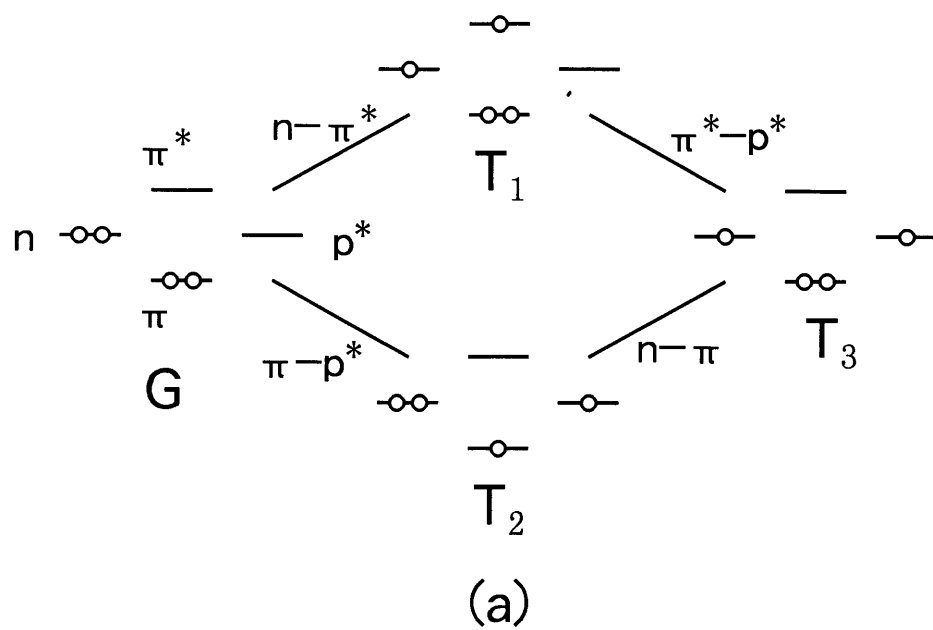


Figure 2. Mechanisms of (a) the electron delocalization from n to p^* orbital and (b) the polarization of the double bond.

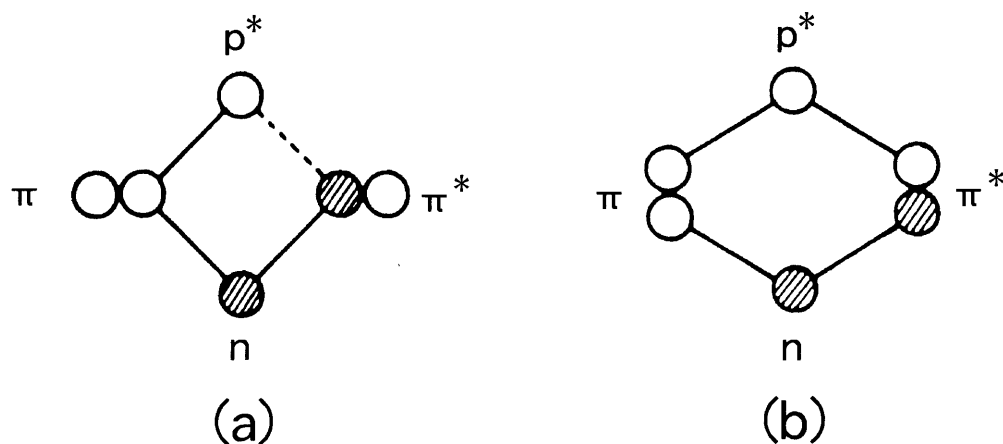


Figure 3. Cyclic orbital interactions: (a) phase discontinuity in the cross-substituted vinylcarbenes; (b) phase continuity in the linear-substituted vinylcarbenes.

the cyclic $-\text{G}-\text{T}_1-\text{E}-\text{T}_2-$ or $-\pi-p^*-\pi^*-n-$ interaction.

The identical cyclic orbital interactions are involved in the delocalization and the polarization. The cyclic $-\pi-p^*-\pi^*-n-$ interaction possesses the dual nature; the delocalization from n to p^* and the polarization of the double bond.

The cyclic orbital interactions of component systems are required for effective delocalization to meet the following conditions:²⁰ (1) electron donating orbitals out of phase; (2) electron accepting orbital in phase; (3) donating and accepting orbital in phase. Those which meet the three requirements simultaneously are electron delocalizing or stable. The cyclic orbital interactions are, otherwise, electron localizing or unstable.

In the linear conjugation π and π^* interact with n at one center and with p^* at the other. All relations between the interacting orbitals meet the phase requirements (Figure 3b): the donating π and n orbitals out of phase; the accept-

ing π^* and p^* orbital in phase; the donating n and accepting π^* in phase and the donation π and accepting p^* orbitals in phase. The orbital phase is continuous. The cyclic orbital interaction is electron delocalizing. This is not the case with the cross conjugation (Figure 3a), where π and π^* interact with n and p^* at the same center. The orbital phase is discontinuous. The dotted line indicates the phase relation opposite to the requirements. The cyclic orbital interaction is electron localizing. As a result, the linear conjugation is thermodynamically more preferable than the cross conjugation for the $4e/4p$ systems. The Hückel-Möbius analogy (Table 1) was found to hold.

Vinylcarbenes

The vinylcarbene **3** and **4** are expected to be $4e/4p$ systems in the planar conformation where the carbene centers may provide the conjugation with p^* . The cross-conjugated systems are the α -substituted vinylcarbenes **3**. The linear-conjugated systems are the β -substituted vinylcarbenes **4**. According to the preceding theoretical arguments the β -derivatives are predicted to be more stable. The geometry optimization by ab initio molecular orbital calculations with STO-3G basis set under constraint to C_s symmetry produced the consistent relative energies of the cross and linear isomers. The energy differences (in kcal/mol) are 65.5 for $X = CH_2^-$, 9.8 for $X = NH_2$, 7.7 for $X = OH$, and 6.2 for $X = SH$.

The delocalization in a part of molecule exhibits some influence on the delocalization in other parts. The delocalization of the lone pair electrons to the double bond is expected to promote the delocalization in a whole molecule by the mechanism discussed above. The extra stabilization should be more remarkable in the electron delocalizing systems. The enhanced delocalization from X to C=C stabilizes the electron delocalizing systems more than the electron localizing systems. It follows that the energy difference between the cross and linear isomers increases with the n-orbital energy height and the overlapping between the n and π^* orbitals. From the n-orbital energy or the electronegativities, the relative stabilities are expected to decrease in order of $\text{CH}_2^- > \text{SH} > \text{NH}_2 > \text{OH}$. The result of the calculations is partly different ($\text{CH}_2^- > \text{NH}_2 > \text{OH} > \text{SH}$). This can be attributed to small overlap integrals between the p_π orbitals of carbon and sulfur (0.125 in **3**; 0.132 in **4**) relative to those (> 0.142) between the corresponding atomic orbitals for X = CH_2^- , NH_2 , or OH.

The orbital phase arguments give some suggestion on the molecular geometry. The electron delocalization gives rise to π -bonding of the double bond with the carbene center and X. The distance in question is more shortened in the electron delocalizing or linear isomers. This is consistent with the optimized bond lengths (\AA) in the linear/cross isomers: 1.35/1.51 (CH_2^-), 1.45/1.51 (NH_2), 1.47/1.52 (OH), and 1.48/1.52 (SH) for the C-C bond; 1.33/1.38 (CH_2^-), 1.38/1.41 (NH_2), 1.37/1.40 (OH), and 1.74/1.77 (SH) for the C-X bond. In

addition, the electron delocalization weakens the double bond and makes it longer. The effect is more remarkable in the electron delocalizing or linear isomers. The prediction was confirmed by the optimized bond lengths [linear/cross (Å): 1.47/1.38 (CH_2^-); 1.35/1.33 (NH_2); 1.34/1.33 (OH); 1.34/1.33 (SH)].

The intramolecular electron delocalization usually raises the LUMO energy and lowers the HOMO energy. The electron-delocalizing linear carbenes are then expected to have the LUMO at higher levels or to be weaker electron acceptors. This is supported by the calculated LUMO energy (Figure 4). On the other hand, the HOMO of most of carbenes is n -orbital in the σ plane. As the linear carbenes are expected to have the π -HOMO at lower levels, the HOMO may be the σ -type orbital as usual. In fact, the calculations showed that the HOMO of the linear carbenes **4** is the n_σ -orbital without exception. In the cross carbenes, the electron delocalization is depressed by the orbital phase discontinuity so that the π -HOMO remains high and possibly high above the n_σ -orbital. The calculations showed that the HOMO's of the cross carbenes are the π orbitals for **3** ($\text{X} = \text{CH}_2^-$, NH_2 , and SH) or the n_σ -orbital with the π -HOMO close in energy for **3** ($\text{X} = \text{OH}$). The chemical behaviors of the carbenes of which both frontier orbitals are π -type orbitals have not been explored so far. Unprecedented chemistry is expected for the cross-substituted vinylcarbenes.

We have confined the arguments to the planar vinyl carbenes which are the $4e/4p$ conjugation systems. However,

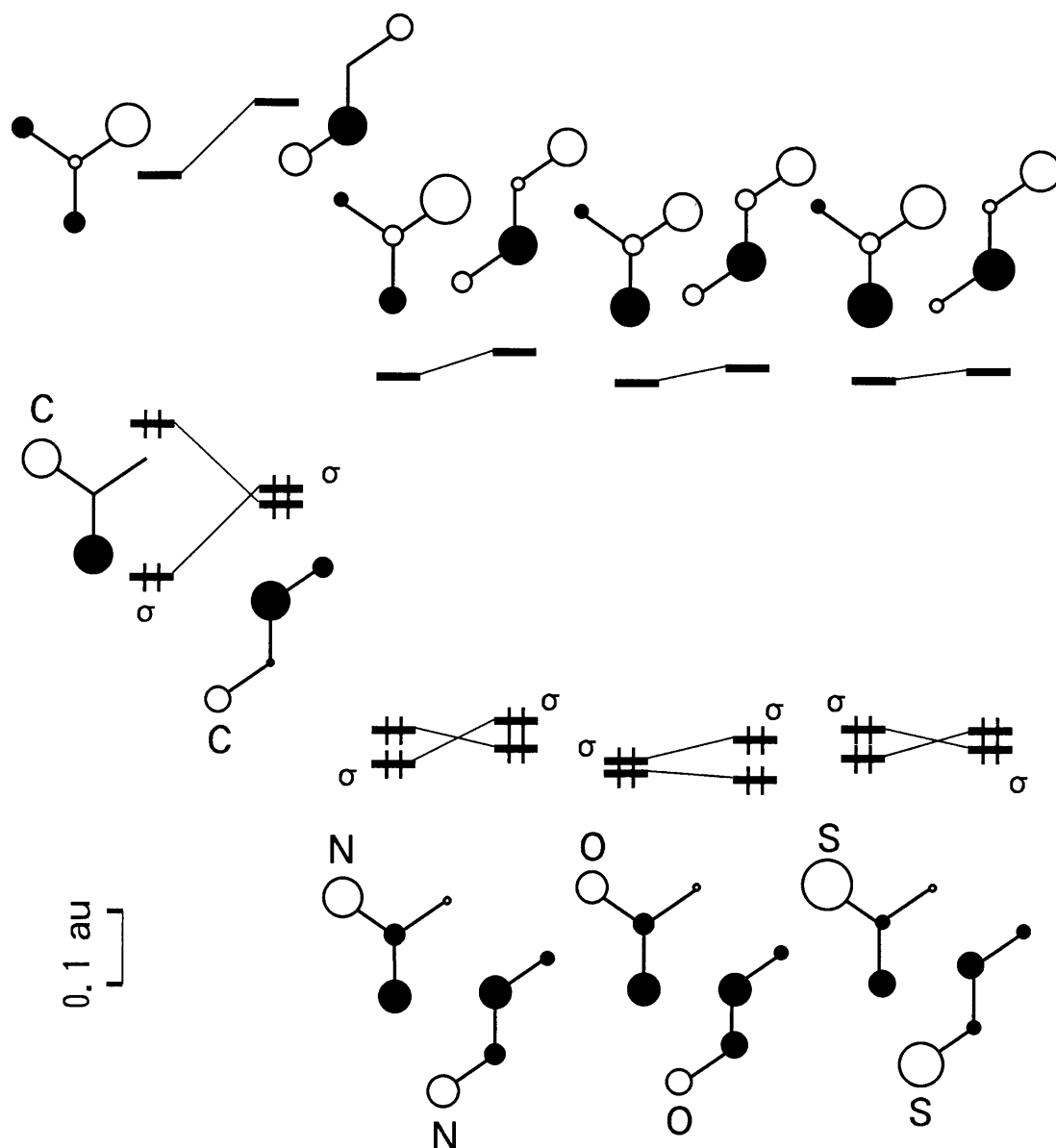


Figure 4. Energies and shapes of frontier MOs of substituted vinylcarbenes.

there remains a possible "vertical" conformation where the lone pair orbital on the carbene center takes part in the conjugation. This conformer is the 6e/4p system likely to be more stable than the 4e/4p system for the cross isomer and less stable for the linear isomer (Table 1). In fact, the pre-

dicted tendency was discerned in the geometry optimization under the constraint that the C–H bond is kept vertical to the molecular plane. The linear-substituted vinylcarbenes preferred the planar confirmation to the extent to which X donates electrons. The energy difference between the vertical and planar conformers is 50.1 kcal/mol for CH_2^- , 17.1 kcal/mol for NH_2 , 13.3 kcal/mol for OH, and 9.7 kcal/mol for SH. These values are significant when the corresponding energy (2.5 kcal/mol) for the parent vinylcarbene ($\text{X} = \text{H}$) is taken into account. The cross-substituted vinylcarbenes' tendency toward the vertical conformation was confirmed in case of the highly electron-donating ability of X. The vertical conformation has lower (by 1.2 kcal/mol) energy than the planar conformers for $\text{X} = \text{CH}_2^-$ and almost the same as the more stable isomer of planar conformation for $\text{X} = \text{NH}_2$. These results can be understood in terms of orbital-phase property. There is a counter intuitive part in the cross isomers. The double bond which accepts more electrons from substituents tends to accept more electrons in the vertical conformation.

Biscarbenes

In the biscarbenes of the present interest there are two carbene centers in conjugation with a double bond. The conformers of the biscarbenes cover all over the possibilities of $2e/4p$, $4e/4p$, and $6e/4p$ conjugations. The planar biscarbene

is 2e/4p conjugation. The conformer with a vertical C–H bond is 4e/4p conjugation. The conformer with both C–H bonds out of plane is 6e/4p conjugation.

For the 2e/4p systems the orbital phase arguments have shown that the electron delocalization prefers the cross to linear conjugation. The calculation produced consistent results. The cross biscarbene of planar structure (C_{2v}) is more stable than any other conformers. The linear counterpart (C_{2h}) is of abnormally high energy (83.5 kcal/mol above the planar cross biscarbene). The geometrical and electronic structures are usual. The linear biscarbene changed from 2e/4p to 4e/4p system during the optimization process. The "optimized" geometry is no longer a double bond in conjugation with the carbene centers but a conjugate system of two double bonds with two σ radical centers on the terminal carbon atoms. The energy and the structures of the linear biscarbene cannot be believed as such. They are the problems beyond the Hartree–Fock level. The anomaly can be understood in terms of the orbital–phase discontinuity in the linear 2e/4p conjugation.

The 4e/4p system has been predicted to prefer the linear conjugation. In fact, the stability relative to the cross isomer (C_1) was estimated to be 5.1 kcal/mol. The calculations showed that this linear 4e/4p biscarbene is the most stable of all conformers of cross and linear biscarbenes. This is by 2.5 kcal/mol more stable than the most stable 2e/4p conformer of the cross biscarbenes.

From the orbital phase property the 6e/4p system has

been predicted to prefer the cross conjugation. The calculations suggested that the $6e/4p$ biscarbenes do not correspond to any equilibrium structure. The geometry optimization started with the structures where the two C–H bonds were vertically bent out of plane in the same or opposite directions. The cross $6e/4p$ biscarbene resulted in the planar $2e/4p$ structure. The linear biscarbene led to acetylenes. The reluctance of the biscarbenes to the $6e/4p$ conjugation may be attributed to the tendency of vinylcarbene toward planar structure.

Conclusion

We applied the concept of the cyclic orbital interaction in noncyclic conjugation to complete the relation of the number of electrons with the delocalizability of electrons in noncyclic conjugated systems of four p-orbitals (Table 1). The $4n+2$ ($n = 0, 1$) π electrons delocalize in the cross-conjugated systems and localize in the linear-conjugated ones. The $4n$ ($n = 1$) π electrons delocalize in the linear-conjugated systems and localize in the cross-conjugated ones. These conclusions remind us of the Hückel–Möbius concept for cyclic polyenes or annulenes. The cross conjugation can be compared to the Hückel conjugation while the linear conjugation can be compared to the Möbius conjugation. The results of ab initio molecular orbital calculations at the Hartree–Fock levels on the substituted vinylcarbenes and conjugated biscarbenes as the $4e/4p$ models and others can be understood

in terms of phase property of the orbitals involved in cyclic interactions for electron delocalization. Although the Hartree–Fock calculations are thought to reveal the fundamental features of these species in the present comparative study, more sophisticated molecular orbital calculations, especially including electron correlation, are necessary for quantitative studies. The clear-cut difference between the cross- and linear-substituted vinylcarbenes or conjugated biscarbenes remains to be experimentally examined in future.

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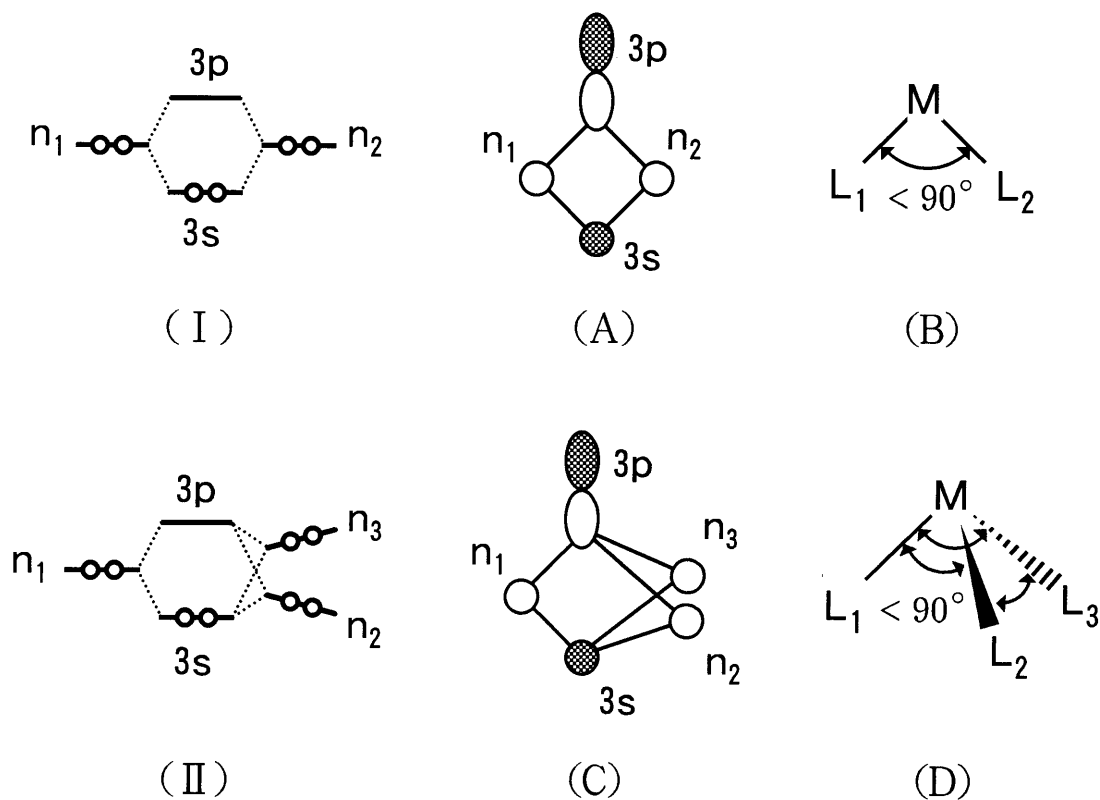
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Chapter 4

Orbital Phase Control of Trigonal Pyramidal Structures of Tricoordinated Metal Complexes

Abstract: Trigonal pyramidal structures of some tricoordinated metal complexes ML_3 ($M = Mg, Al, Si$) are predicted by an orbital phase theory and confirmed by ab initio molecular orbital calculations to have acute L-M-L angles in spite of the steric congestion.

Recently, some metal (M) complexes with two ligands (L_1 and L_2) have been predicted by ab initio molecular orbital calculations to have acute L_1 -M- L_2 angles.^{1, 2} Angles between the hybrid orbital axes cannot be less than 90° in the s-p hybridization. The anomaly has been proposed to be controlled by the orbital phase continuity-discontinuity properties.¹ The dicoordinated complexes with the $(3s)^2(3p)^0$ configuration of the metals involve a cyclic interaction of the 3s and 3p atomic orbitals and the ligand orbitals n_1 and n_2 (I), while the complexes assume noncyclic L-M-L



geometry. The cyclic $-3s-n_1-3p-n_2-$ interaction in the non-cyclic systems satisfies the phase continuity requirements³ (A) at the geometry (B) with an acute angle, where one lobe of $3p$ interacts with both n_1 and n_2 . Here, we designed tricoordinated complexes ML_3 with acute $L-M-L$ angles.

In the tricoordinated complexes an additional orbital n_3 of the ligand L_3 interacts with $3s$ and $3p$ (II). The three cyclic interactions $-3s-n_1-3p-n_2-$, $-3s-n_2-3p-n_3-$, and $-3s-n_3-3p-n_1-$ are involved. Each of the cyclic interactions meets the orbital phase requirements³ when the three n orbitals interact with the same lobe of a single $3p$ orbital (C). The electron-donating n orbitals are out of phase with the donating $3s$, and in phase with the accepting $3p$ orbital. This sug-

gests that the L–M–L angles should be acute (D).

The orbital phase continuity requirements are valid for the α - and β -spin spaces individually.⁴ The prediction is applicable to open-shell complexes, e.g., the $(3s)^1(3p)^0$ configurations.

Geometries of ML_3 were optimized⁵ by the R(O)HF method with the 6–31G basis set under the constraint of the C_3 or C_s symmetry. The results are summarized in Table 1.

The prediction was confirmed by the acute C–M–C angles of $^+Al(CO)_3$, $Al(CO)_2(CN)$, and $^+Si(CO)_2(CN)$ with the metal $(3s)^2(3p)^0$ configuration.⁶ Figure 1 shows the dependences of the total energies and the Al–C distances of $^+Al(CO)_3$ on the C–Al–C angle. The decrease in the angle stabilizes the complex and shortens the Al–C distances.⁷ The cyclic orbital interaction (C) contains the n–3p interaction or the electron delocalization from L to M. The shortening of the Al–C distance may result from the electron delocalization enhanced by the phase continuity.

The total wave functions were decomposed into various electronic configurations, e.g., the locally-excited $3s \rightarrow 3p$ configuration $E(3s \rightarrow 3p)$ and the electron-transferred $n \rightarrow 3p$ configuration $T(n \rightarrow 3p)$.⁸ The cyclic orbital interaction (C) involves the atomic polarization of the metal (mixing of $E(3s \rightarrow 3p)$) and the electron delocalization from L to M (mixing of $T(n \rightarrow 3p)$). The coefficient ratio of E or T to the ground configuration G (C_E/C_G or C_T/C_G), or the measures^{3b} of the atomic polarization and the electron delocalization are plotted in Figure 2.⁹ The $3p_z$ orbital is on the C_3 axis, and L_1 lies

Table 1. Optimized Geometries

	metal state	C-M-C angle/degree		M-CO distance/ \AA	
		OC-M-CO	OC-M-CN	M-CO	M-CN
$^+ \text{Mg}(\text{CO})_3$	$(3s)^1(3p)^0$	86.2		2.082	
$^{+2} \text{Al}(\text{CO})_3$	$(3s)^1(3p)^0$	95.1		2.227	
$^+ \text{Al}(\text{CO})_3$	$(3s)^2(3p)^0$	82.2		3.224	
$\text{Al}(\text{CO})_2(\text{CN})$	$(3s)^2(3p)^0$	82.0	72.8	3.531	2.064
$^+ \text{Si}(\text{CO})_2(\text{CN})$	$(3s)^2(3p)^0$	83.6	86.7	2.377	1.896

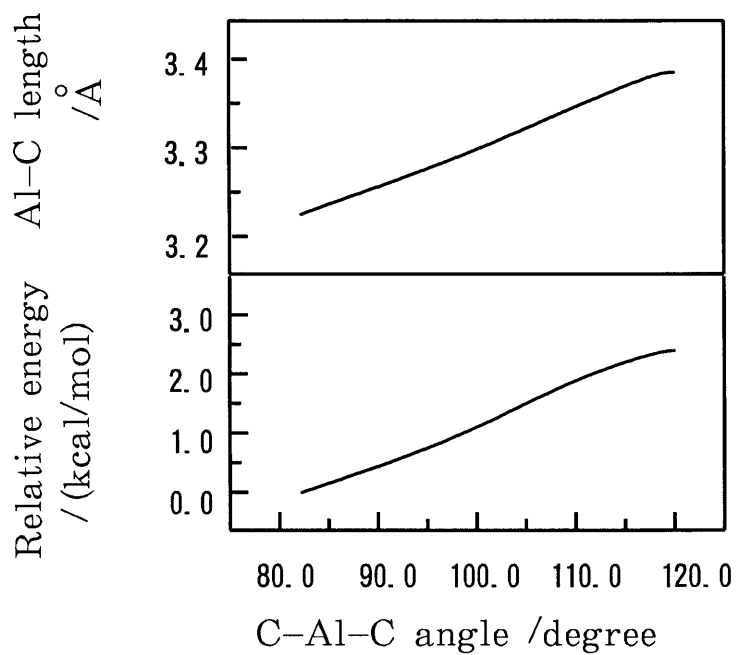


Figure 1. Structural and energetical changes.

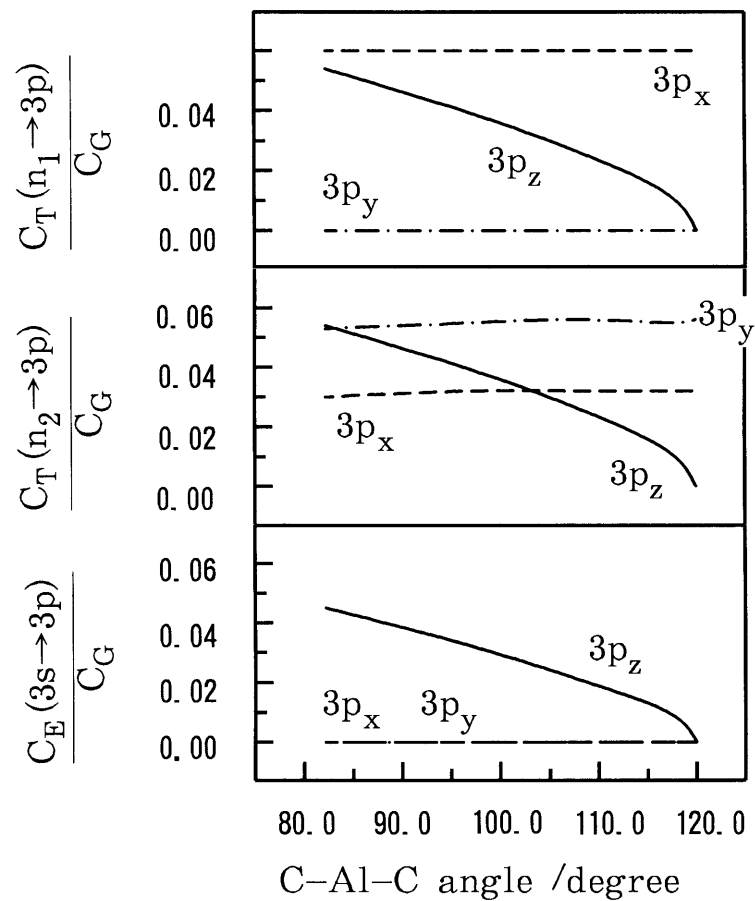


Figure 2. Atomic polarization (C_E/C_G) and electron delocalization (C_T/C_G).

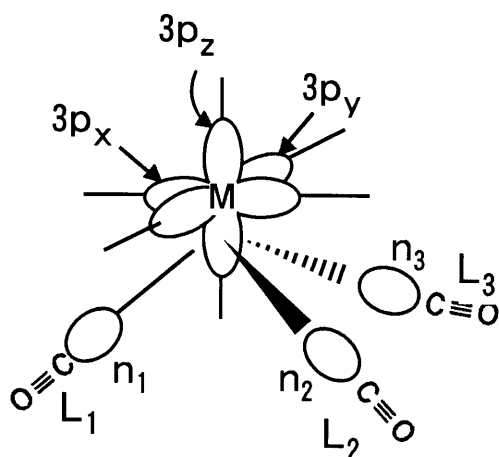


Figure 3. Definition of orbitals.

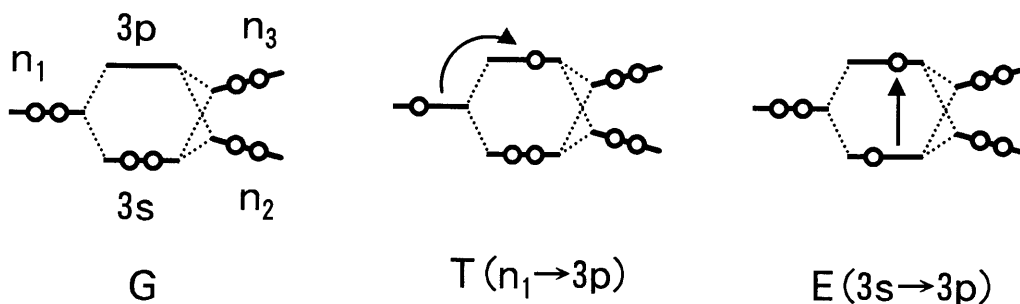


Figure 4. Electron configurations.

on the xz plane (Figure 3). The polarization and the delocalization involving $3p_z$ are enhanced with the decrease in the angle. The result supports the orbital phase prediction that the cyclic interaction at the same lobe of a p orbital stabilizes the complexes.

The angle in $^+Mg(CO)_3$ is also acute (86.2°) in agreement with the prediction for the metal $(3s)^1(3p)^0$ configuration. However, $^{+2}Al(CO)_3$ with the same configuration has a

little obtuse angle. The exception may be caused by insufficient stabilization due to the reduced number of electrons involved in the cyclic interaction.

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6. The acute O-Al-O angles of trihydrated aluminum clusters were reported: Watanabe, H. ; Aoki, M. ; Iwata, S. *Bull.*

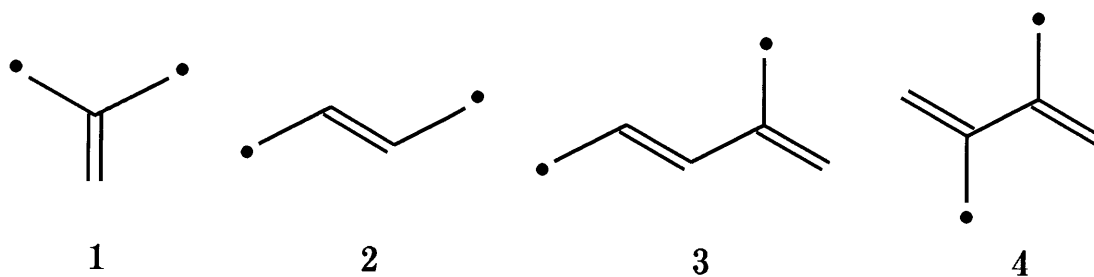
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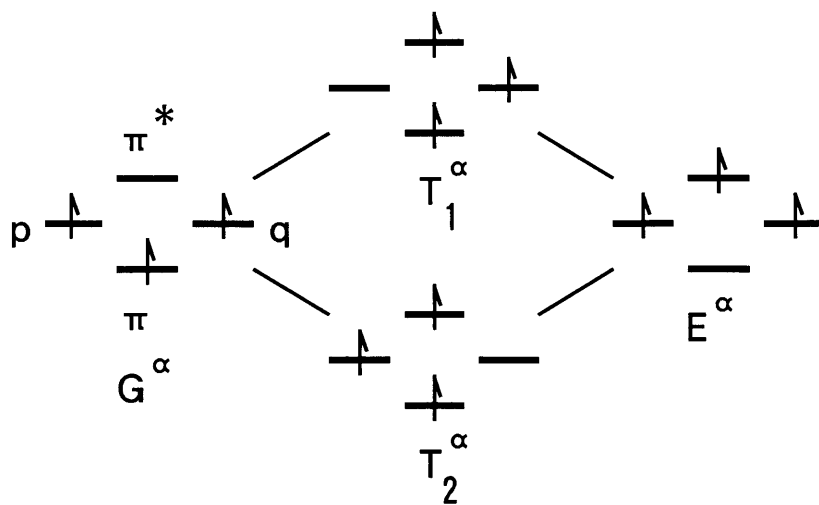
Chapter 5

Orbital Phase Continuity Requirements in Triplet States

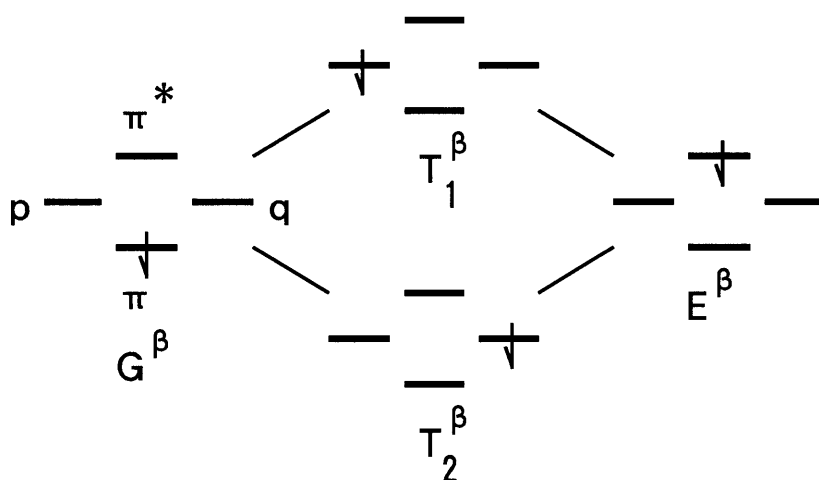
Abstract: Orbital phase continuity requirements were derived for stabilizing triplet states, and successfully applied to non-cyclic conjugated diradicals.

Triplet states of molecules are important intermediates in photochemical processes.¹ Triplet diradicals receive an increasing interest as prototypes of high-spin molecules for molecular magnetic materials.² In this chapter we will present an orbital phase theory for the stabilities of triplet states and apply it to some conjugated diradicals 1–4.





(a) α -spin



(b) β -spin

Scheme 1

In **1**–**4**, two radical centers do not effectively interact with each other, but with an intervening conjugated coupler. The coupler is an ethylene unit in **1** and **2**, and a butadiene unit in **3** and **4**. The modes of connection of the radical centers and the couplers are different between **1** and **2**, and **3** and **4**.

The mechanism of electron delocalization and polarization is illustrated in Scheme 1. An α -spin electron occupies each of the radical orbitals, p and q, and the HOMO (π) of the coupler in the ground configuration (G^α). The electron in one of the radical centers (p) shifts to the LUMO (π^*) of the coupler through the interaction of G^α and the transferred configuration (T_1^α). The $G^\alpha-T_1^\alpha$ interaction is approximated to the $p-\pi^*$ interaction. The resulting electron hole in the radical center p is supplied with an electron from π of the coupler through the interaction of T_1^α and the locally-excited configuration (E^α), or the $p-\pi$ interaction. The $\pi-p-\pi^*$ interaction is involved in the delocalization-polarization process. There is another process involving the $G^\alpha-T_2^\alpha-E^\alpha$ or $\pi-q-\pi^*$ interaction. As a result, cyclic $-G^\alpha-T_1^\alpha-E^\alpha-T_2^\alpha-$ or $\pi-p-\pi^*-q-$ interaction occurs.

For effective occurrence of the cyclic interaction, simultaneous bonding properties are required between any pair of configuration:

$$S(G^\alpha, T_1^\alpha)S(T_1^\alpha, E^\alpha)S(E^\alpha, T_2^\alpha)S(T_2^\alpha, G^\alpha) > 0 \quad (1)$$

where S is an overlap integral between configurations. The inequality is rewritten as

$$s(p, \pi^*)s(\pi, p)s(q, \pi^*)s(\pi, q) > 0 \quad (2)$$

where s denotes orbital overlap integral.

Delocalization-mechanism of β -electrons is shown in Scheme 1b. An electron shifts from π to p through the $G^\beta-T_1^\beta$ or $\pi-p$ interaction. The electron then shifts to π^* through the $T_1^\beta-E^\beta$ or $p-\pi^*$ interaction. The $G^\beta-T_1^\beta-E^\beta$ or $\pi-p-\pi^*$ interaction is involved. The other process involves the $G^\beta-T_2^\beta-E^\beta$ interaction or the $\pi-q-\pi^*$ interaction. The cyclic $-G^\beta-T_1^\beta-E^\beta-T_2^\beta-$ or $\pi-p-\pi^*-q-$ interaction similarly occurs in the β -spin delocalization-polarization process. The same inequality (2) was obtained.

The inequality requirements can easily be seen to be equivalent to simultaneous satisfaction of the orbital phase continuity conditions: 1) the electron donating orbitals out of phase; 2) the accepting orbitals in phase; 3) the donating and accepting orbitals in phase. The p and q orbital at the radical centers are the donating orbitals for α -spin and the accepting orbitals for β -spin. The phase conditions are essentially the same as those for cyclic³ and noncyclic⁴ closed-shell molecules.

The diradicals **1** and **3** meet the phase requirements in both spin spaces. The orbital phase is continuous. This is not the case with their isomers, **2** and **4**. The phase is discontinuous. Consequently, triplet states of **1** and **3** are thermodynamically stable relative to **2** and **4**, respectively. This agrees with known relative stabilities found in literatures.⁵

We carried out ab initio UHF calculations⁶ on the triplet states of these diradicals. The total wave functions were subjected to the open-shell configuration analysis. The results

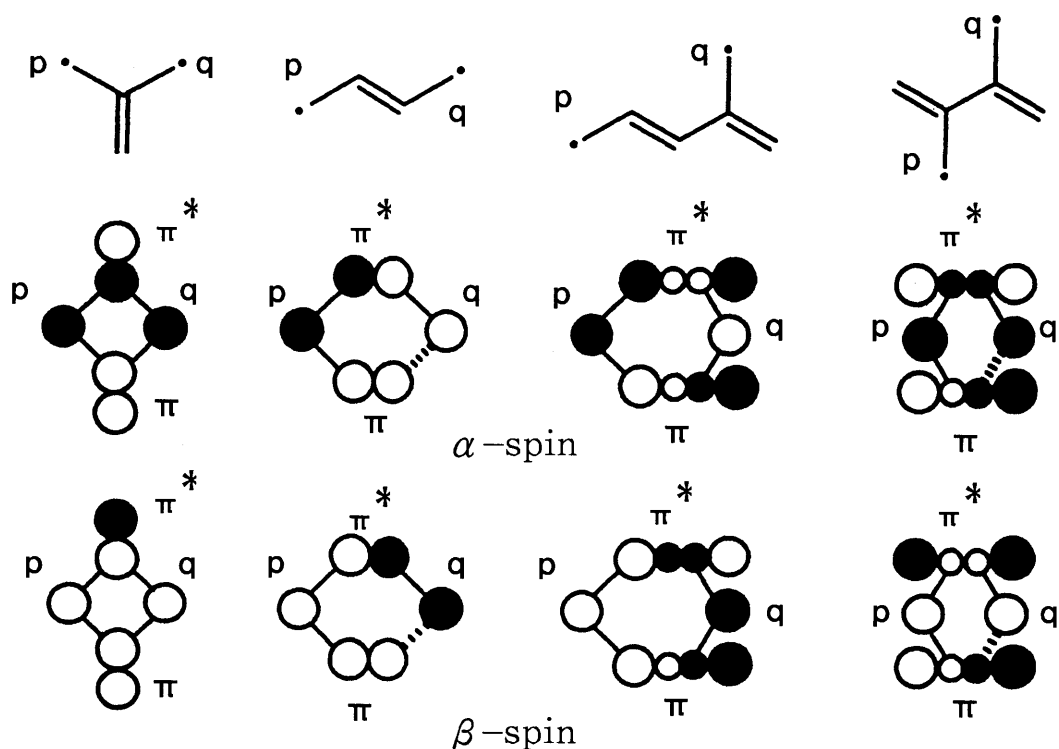


Table 1. Coefficient Ratios of Locally-Excited and Electron-Transferred Configurations to the Ground Configuration

triplet diradical	E^α	T_1^α	T_2^α	E^β	T_1^β	T_2^β
1	0.49	0.25	0.25	0.50	0.25	0.25
2	0.00	0.15	0.15	0.00	0.13	0.13
3	0.62	0.30	0.17	0.60	0.30	0.17
4	0.00	0.26	0.26	0.00	0.27	0.27

(Table 1) supported the orbital phase predictions. Contributions of the local-excitation of both spins are significant in **1** (0.49 for E^α and 0.50 for E^β), whereas absent in **2**. Electron delocalization or mixing of the transferred configurations also prefers **1** (0.25 for both spins) to **2** (0.15 for α and 0.13

for β -spin). This is understood as the results of the orbital phase continuity (1) and discontinuity (2). The effect of the orbital phase is outstanding in the polarization rather than the delocalization. There are great contributions from the polarization in 3, but not at all in 4. This is also understood due to the continuity (3) and discontinuity (4) of orbital phase.

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Chapter 6

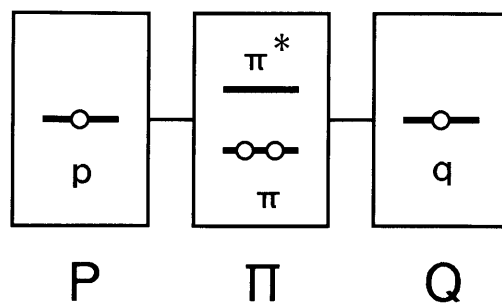
Orbital Phase Control of Stabilities of π -Conjugated Diradicals

Abstract: The concept of orbital phase continuity–discontinuity was applied to π -conjugated diradicals where two radical centers (P and Q) indirectly interact with each other through π -bonds (Π). Cyclic orbital interactions are involved in spin polarization and delocalization in the noncyclic π -conjugated diradicals. Relative stabilities of singlet isomers, those of triplet ones, and spin multiplicities of ground states were shown to be predicted by the orbital phase properties.

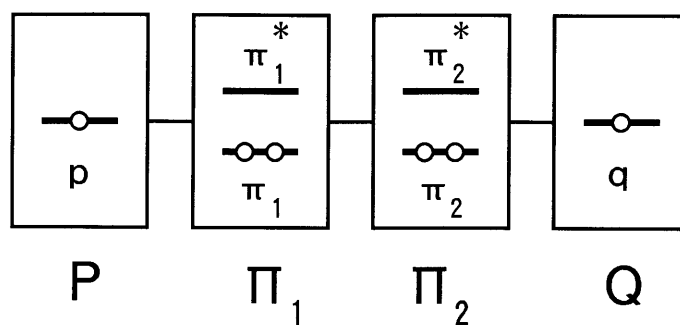
The orbital phase theory entered a new stage when cyclic orbital interactions were revealed to be involved in molecular systems of noncyclic geometries.^{1–8} Relative stabilities of cross vs. linear conjugated systems were shown to be controlled by the orbital phase continuity–discontinuity properties.^{1–5} The orbital phase theory for the noncyclic systems was found to account for regioselectivities of organic

reactions⁶ and for abnormally acute L–M–L angles in ML_2 ⁷ and ML_3 ⁸ complexes. Stabilities of wide variety of the closed-shell systems were shown to be determined by the orbital phase properties.

Diradicals are intermediates in photochemical reactions⁹ and prototypes of molecular magnetic materials.¹⁰ Stability of the intermediate diradicals is one of the essential factors for determining the reaction paths. Spin multiplicities of the ground states are critical for the magnetism. The present work was undertaken to develop an orbital phase theory for open-shell systems or singlet and triplet π -conjugated diradicals. We derived the orbital phase requirements for stabilizing the diradicals. The theory was successfully applied to predicting relative stabilities of singlet (triplet) isomers. Also, the theory was found to be useful for predicting the spin multiplicity of the ground states of both the alternant and non-alternant diradicals. The theories for the spin preference have been developed by Borden and Davidson¹¹ and by Ovchinnikov.¹² The application is, however, limited to alternant diradicals. The present phase theory unequivocally gave the spin preference of the diradicals in which the singlet states are predicted by Borden and Davidson to be always lower than the triplet. Our predictions were in agreement with the Radhakrishnan's rule¹³ for the spin preference. The orbital phase theory is shown to be applicable to both the relative stability of the isomers and the spin preference.



(a)



(b)

Figure 1. Noncyclic π -conjugated systems with two radical centers intervened by (a) one and (b) two π -bonds.

Orbital Phase Continuity Requirements

We studied noncyclic conjugated diradicals (Figure 1a) where two radical centers (P and Q) do not directly interact with each other, but through a π -bond (Π). We derive orbital phase requirements for effective delocalization of electrons or spins and polarization of the π -bond.

Triplet States.¹⁴ The mechanism of delocalization and polarization of α -spin electrons in a triplet state of the P- Π -Q system is schematically represented in Figure 2a.¹⁵ One

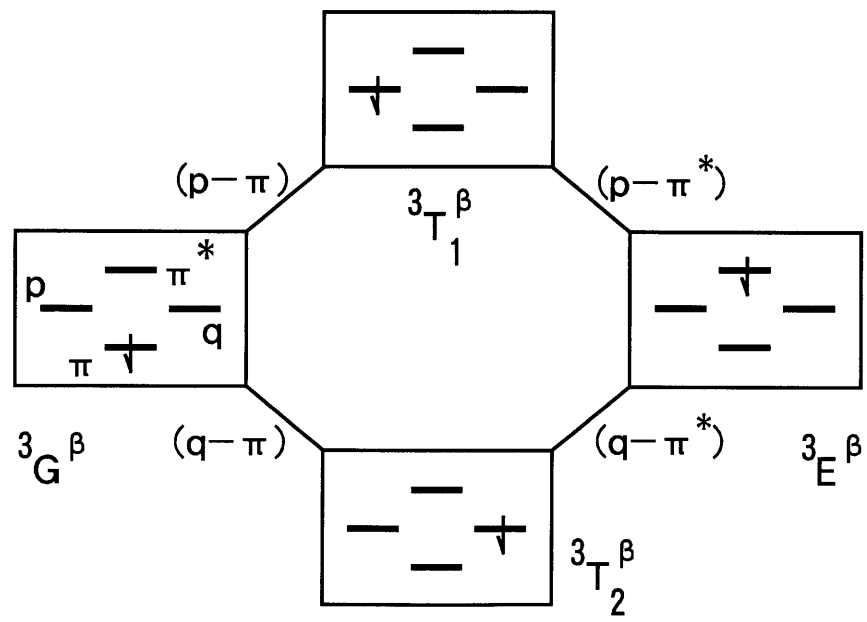
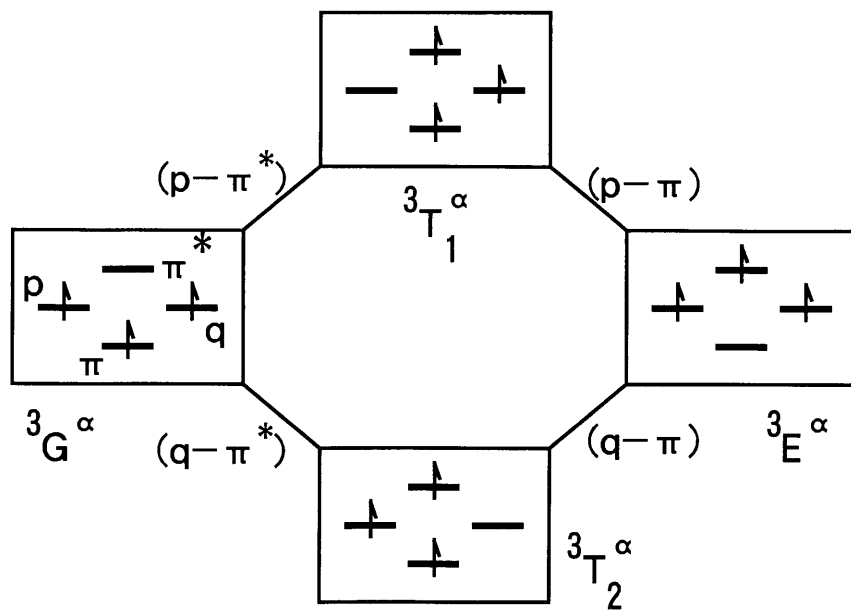


Figure 2. Delocalization-polarization mechanisms of (a) α - and (b) β -spin electrons in the triplet states of the P- Π -Q system.

electron occupies each of the radical orbitals (p and q) and a bonding π -orbital (π) of the π -bond in the ground configuration ${}^3G^a$. The electron in p shifts to an antibonding π -orbital (π^*) of the π -bond through the interaction of the ground configuration with the transferred configuration ${}^3T_1^a$. Mixing of the transferred configurations gives rise to the electron delocalization from P to Π . The configuration interaction is approximated to the $p-\pi^*$ interaction. The resulting electron hole in p is supplied with an electron by π through the interaction of the transferred configuration with a locally-excited configuration ${}^3E^a$. Mixing of the locally-excited configuration polarizes Π . The interaction of the transferred and excited configuration is approximated to the $\pi-p$ interaction. Thus, the ${}^3G^a-{}^3T_1^a-{}^3E^a$ or $\pi-p-\pi^*$ interaction is involved in the delocalization-polarization process. There is another process through the other radical orbital q. This involves the ${}^3G^a-{}^3T_2^a-{}^3E^a$ or $\pi-q-\pi^*$ interaction. As a result, a cyclic ${}^3G^a-{}^3T_1^a-{}^3E^a-{}^3T_2^a-$ or $-\pi-p-\pi^*-q-$ interaction (Figure 3a) occurs.

For effective occurrence of the cyclic configuration interaction, simultaneous bonding properties are required between any pair of them:

$$S({}^3G^a, {}^3T_1^a)S({}^3T_1^a, {}^3E^a)S({}^3E^a, {}^3T_2^a)S({}^3T_2^a, {}^3G^a) > 0 \quad (1)$$

where S is an overlap integral between the configurations. The inequality is rewritten (see Appendix I) as

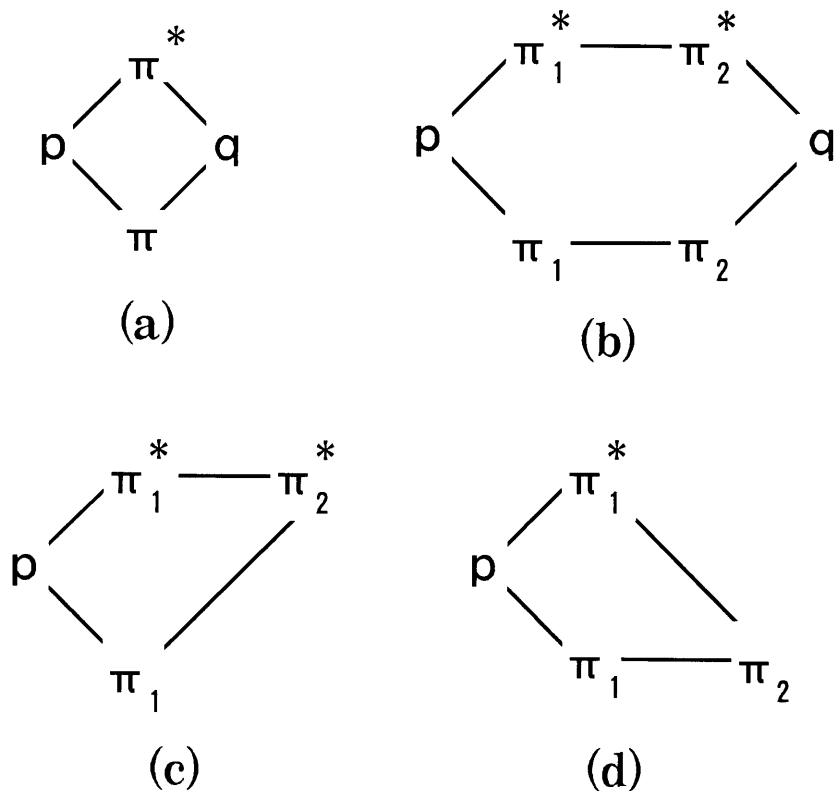


Figure 3. Cyclic orbital interactions involved in the di-radicals: (a) four-orbital interaction in the P- Π -Q system; (b) six-orbital interaction in the P- Π_1 - Π_2 -Q system; (c and d) interactions in the substructure P- Π_1 - Π_2 .

$$s(p, \pi^*)s(\pi^*, q)s(q, \pi)s(\pi, p) > 0 \quad (2)$$

where s denotes an orbital overlap integral.

The requirement is included in simultaneous satisfaction of the orbital phase continuity conditions: i) the electron donating orbitals out of phase; ii) the accepting orbitals in phase; iii) the donating and accepting orbitals in phase. The donating and accepting orbitals are occupied and unoccupied

by electrons in the ground configurations, respectively. The radical orbitals p and q are electron-donating for α -spin. The phase conditions are essentially the same as those for noncyclic closed-shell molecules.¹ If the requirements are satisfied or the orbital phase is continuous, the delocalizations and the polarizations effectively occur.

Delocalization-polarization mechanism of a β -spin electron is shown in Figure 2b. One electron occupies π in the ground configuration ${}^3G^\beta$. The electron shifts to p through the interaction of the ground configuration with a transferred configuration ${}^3T_1^\beta$ or π -p interaction. The electron further shifts to π^* through the interaction of the transferred configuration with a locally-excited configuration ${}^3E^\beta$ or p- π^* interaction. The ${}^3G^\beta$ - ${}^3T_1^\beta$ - ${}^3E^\beta$ or π -p- π^* interaction is involved in the delocalization-polarization process. Mixing of the transferred and excited configuration gives rise to the electron delocalization from Π to P and the polarization of Π , respectively. There is another delocalization-polarization process through the other radical orbital q, which involves the ${}^3G^\beta$ - ${}^3T_2^\beta$ - ${}^3E^\beta$ or π -q- π^* interaction (Figure 3a). A cyclic ${}^3G^\beta$ - ${}^3T_1^\beta$ - ${}^3E^\beta$ - ${}^3T_2^\beta$ - or $-\pi$ -p- π^* -q- interaction occurs. The same inequality 2 is required (see Appendix I). The requirement for β -spin is also included in the orbital phase continuity conditions. In this case the radical orbitals, p and q, are electron-accepting.

Singlet States. Delocalization-polarization mechanism of α -spin electrons in a singlet state of the P- Π -Q system is

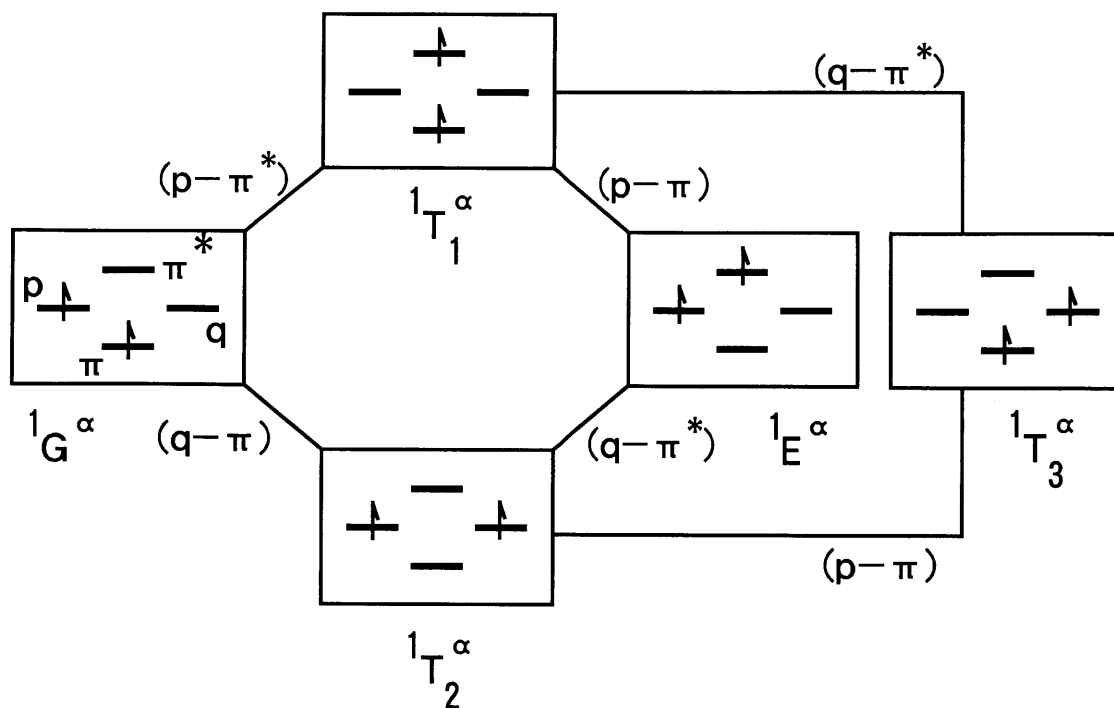


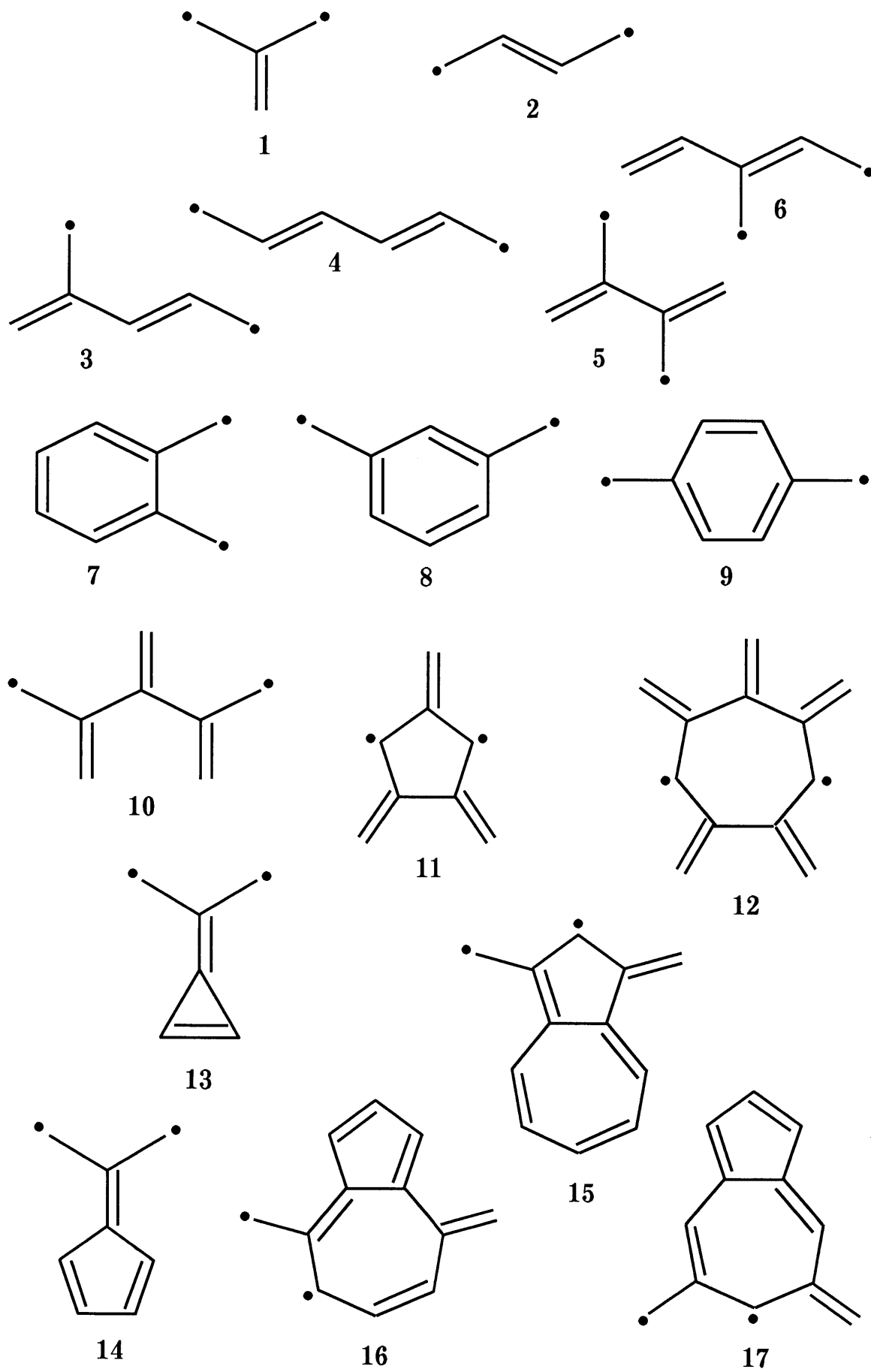
Figure 4. Delocalization-polarization mechanisms of α -spin electrons in the singlet states of the P- Π -Q system.

shown in Figure 4.¹⁵ The electrons occupy π and one radical orbital (p) in the ground configuration ${}^1G^\alpha$. The electron shifts from p to π^* through the interaction of the ground configuration with a transferred configuration ${}^1T_1^\alpha$ or $p-\pi^*$ interaction. The resulting electron hole in p is supplied with an electron by π through the interaction of the transferred configuration with a locally-excited configuration ${}^1E^\alpha$ or $\pi-p$ interaction. The ${}^1G^\alpha-{}^1T_1^\alpha-{}^1E^\alpha$ or $\pi-p-\pi^*$ interaction is involved. The other process involves the ${}^1G^\alpha-{}^1T_2^\alpha-{}^1E^\alpha$ or $\pi-q-\pi^*$ interaction. A cyclic ${}^1G^\alpha-{}^1T_1^\alpha-{}^1E^\alpha-{}^1T_2^\alpha-$ or $-\pi-p-\pi^*-q-$ interaction (Figure 3a) occurs. We obtain (see Appendix I)

$$(-1)s(p, \pi^*)s(\pi^*, q)s(q, \pi)s(\pi, p) > 0 \quad (3)$$

The cyclic orbital interaction is involved in the delocalization from p to q. The electron in π^* in the transferred configuration ${}^1T_1^\alpha$ farther shifts to q through the interaction of the configuration with another transferred configuration ${}^1T_3^\alpha$ or q $-\pi^*$ interaction. The electron hole in π in the transferred configuration ${}^1T_2^\alpha$ is supplied with an electron by p through the interaction of the transferred configuration with ${}^1T_3^\alpha$ or p $-\pi$ interaction. Mixing of the transferred configuration ${}^1T_3^\alpha$ into the ground one provides an ionic term characteristic to the singlet state. The inequality 3 is obtained. Note that the sign of the left side of the inequality is opposite to that of the inequality 2. The phase continuity properties of the singlet and triplet states of a given diradical are opposite to each other. The requirement is again included in the orbital phase continuity conditions. One radical orbital p is electron-donating and the other q is accepting. The same inequality 3 is obtained for β -spin.

Relative Stability of Trimethylenemethane and Butadiene Diradical. The orbital phase theory are applied to trimethylenemethane (**1**, TMM) and butadiene diradical (**2**, BD diradical) in the triplet states. The cyclic orbital interaction involved in **1** meets the phase requirements in both spins (Figure 5). For α -spin the electron donating radical orbitals p and q can simultaneously be out of phase with the



donating orbital π and in phase with the accepting π^* . For β -spin the accepting radical orbitals p and q can be in phase with the donating π the accepting π^* . The orbital phase is continuous. This is not the case with its isomer **2**. The orbital phase is discontinuous. Therefore, **1** is predicted to be thermodynamically favored relative to **2**. This is well-known relative stability (Table 1).¹⁶⁻¹⁸ Difference of the energies of the unstable isomer from the stable one, ΔE_i , is 15.3 kcal/

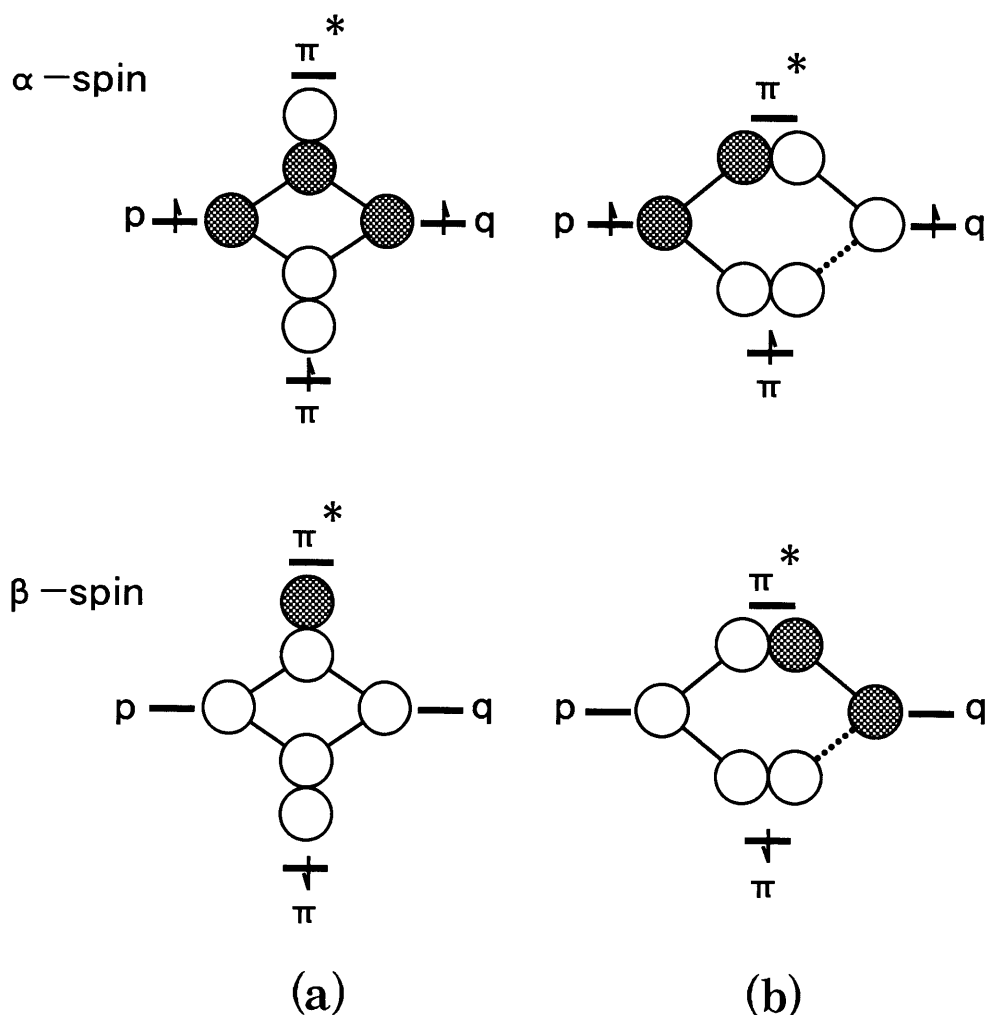


Figure 5. The orbital phase continuity of **1** (a) and the discontinuity of **2** (b) in the triplet states.

mol in the MCSCF(4, 4)¹⁹ level.

In the singlet states **2** meets the phase requirements simultaneously, while **1** does not (Figure 6). Let the spins of the electrons in the radical orbitals p and q be α and β , respectively. For α -spin, p is an electron donating orbital and q is an accepting. The donating orbitals p and π out of phase with each other allows any other pairs of interacting orbitals to be in phase in **2** as required (Figure 6b). The orbital phase is continuous. In **1** the out-of-phase combined p and π break the phase continuity requirements between at least one pair of orbitals (π and q in Figure 6a).

The phase continuity in singlet diradicals of Kekule' molecules does not indicate the stability of the diradicals, but that of the corresponding closed-shell ground state. The singlet diradicals of Kekule' molecules are excited states. It follows that the phase continuity of singlet diradicals of

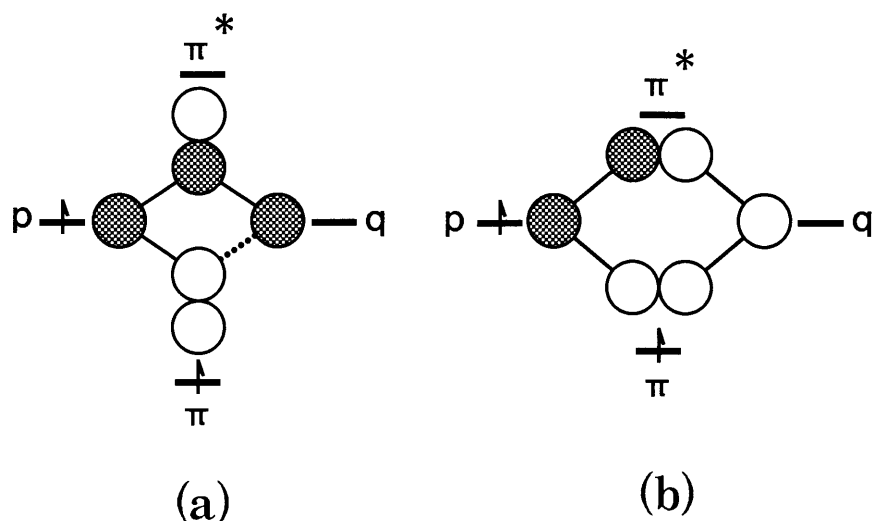


Figure 6. The orbital phase discontinuity of **1** (a) and the continuity of **2** (b) in the singlet states.

Table 1. Total Energies (hartrees) and Relative Energies (kcal/mol) of Isomers (ΔE_i^a) and Energy Differences between the Singlet and the Triplet States (ΔE_m^b) of the Diradicals Obtained by the MCSCF Geometry Optimizations^c

	triplet			singlet			ΔE_m
	state	total	ΔE_i	state	total	ΔE_i	
1	$1^3A'_2$	-153.0321	0.0	1^1A_1	-152.9984	0.0	21.1
2	1^3B_u	-153.0077 ^d	15.3	$2^1A_g^e$	-152.8959 ^d	64.3	
3	$1^3A'$	-229.0257	0.0	$1^1A'$	-229.0055	3.9	12.7
4	1^3B_u	-229.0141	7.3	$2^1A_g^e$	-228.9239	55.1	
5	1^3B_{2u}	-229.0068	11.9	1^1A_g	-229.0117	0.0	-3.1
6	1^3A_1	-228.9941	19.8	$2^1A_1^e$	-228.8635	93.0	
				$1^1B_2^e$	-228.8949	73.3	
7	1^3B_2	-303.8454	6.6	$2^1A_1^e$	-303.7235	72.5	
8	1^3B_2	-303.8559	0.0	1^1A_1	-303.8391	0.0	10.5
9	1^3B_{2u}	-303.8369	11.9	$2^1A_g^e$	-303.7153	77.7	
10	1^3B_2	-304.9220		1^1A_1	-304.9219		0.06
		-304.9670 ^f			-304.9661 ^f		0.56 ^f

^aRelative to the energies of the most stable isomers. ^bA positive value indicates that the triplet state is more stable than the singlet. ^cThe MCSCF (4, 4)/STO-3G method for **1** and **2**, and the MCSCF (6, 6)/STO-3G for the other molecules were employed. ^dRef. 18. ^eLow-lying singlet excited state. ^fResult of the MCSCF (8, 8)/STO-3G optimization.

Table 1. (Continued)

	triplet			singlet			ΔE_m
	state	total	ΔE_i	state	total	ΔE_i	
12	1^3B_2	-455.6587		1^1A_1	-455.6620		-2.0
15	1^3B_2	-454.5882		1^1A_1	-454.5100		49.1
16	1^3B_2	-454.5560		1^1A_1	-454.5340		13.8
17	1^3B_2	-454.5772		1^1A_1	-454.5366		25.5

Table 2. C_T/C_G and C_E/C_G Values^a for **1** and **2**

	triplet			singlet				
	state	$\frac{C_T(\Pi \rightarrow P)}{C_G}$	$\frac{C_T(P \rightarrow \Pi)}{C_G}$	$\frac{C_E(\Pi)}{C_G}$	state	$\frac{C_T(\Pi \rightarrow P)}{C_G}$	$\frac{C_T(P \rightarrow \Pi)}{C_G}$	$\frac{C_E(\Pi)}{C_G}$
1	$1^3A'_2$	0.210	0.334	0.700	1^1A_1	0.126	0.140	0.015
2	1^3B_u	0.139	0.148	0.243	2^1A_g	0.287	0.254	0.873

^aAbsolute values of the coefficient ratios indicating the electron delocalizability. The MCSCF(4,4) wave functions were employed for the analyses.

Kekulé molecules indicates the destabilization of the diradicals. The phase continuity in **2** and the phase discontinuity in **1** imply that **2** should be less stable than **1**. This agrees with the previous calculations.^{17, 18}

The method for evaluating the electron delocalization from bonds to bonds and the polarization of bonds has been useful for investigating electronic structures of closed-shell systems.^{2, 4, 8, 20} We developed a method for open-shell molecules (see Appendix II) to examine the preceding qualitative theory in a numerical manner. The delocalization and the polarization were estimated² as C_T/C_G and C_E/C_G , i.e., the ratios of coefficients of the transferred and the locally-excited configurations to that of the ground configuration. The MCSCF(4, 4) wave functions were employed in analyzing the electronic structures. The results (Table 2) confirm the orbital phase theory. For the triplet states the polarization or mixing of the configuration of the local excitation of the π -bond is significant in **1** ($C_E(\Pi)/C_G = 0.700$) relative to **2** (0.243). The delocalization or mixing of the transferred configuration also prefers **1** ($C_T(P \rightarrow \Pi)/C_G = 0.210$, $C_T(\Pi \rightarrow P)/C_G = 0.334$) to **2** (0.139, 0.148). For the singlet states the significant delocalizations and polarization in **2** ($C_T(P \rightarrow \Pi)/C_G = 0.287$, $C_T(\Pi \rightarrow P)/C_G = 0.254$, and $C_E(\Pi)/C_G = 0.873$) were evaluated for the excited state relative to those (0.126, 0.140, and 0.015) for **1**.

The cyclic orbital interactions were shown to be involved in the noncyclic P- Π -Q systems. The relative stabilities of isomers of the singlet (triplet) diradicals were shown to be

controlled by the orbital phase continuity–discontinuity properties of the cyclic interactions.

Relative Stabilities of Isomers

C₆H₈ Diradicals (3–6). We apply the orbital phase theory to extended conjugated diradicals with one more π -bond (P– Π_1 – Π_2 –Q, Figure 1b). The radical orbital p interacts with bonding (π_1) and antibonding (π_1^*) orbitals of the neighboring π -bond Π_1 , the other q with those (π_2 and π_2^*) of Π_2 . There are π_1 – π_2 and π_1^* – π_2^* interactions between the π -bonds. Thus the cyclic six-orbital – π_1 –p– π_1^* – π_2^* –q– π_2 – interaction (Figure 3b) is involved.

In the triplet state of the diradical **3** the cyclic six-orbital interaction is favored by the phase continuity (Figure 7a). The diradical **3** is predicted to be a stable triplet isomer. The six-orbital phase is discontinuous in **4** and **5** (Figure 7b and 7c, respectively). These diradicals are unstable triplets. The diradical **6** is a vinyl derivative of the P– Π –Q system with the BD diradical unit, but not a P– Π_1 – Π_2 –Q system. The four-orbital phase is discontinuous in the BD diradical unit (Figure 5b). The phase restriction is more strict in **6** more than **4** and **5** since the radical centers are closer to each other. The diradical **6** is the least stable isomer. The relative stability is predicted to decrease in the order of **3** > **4**, **5** > **6**.

Relative stability of **4** and **5** is determined by the cyclic

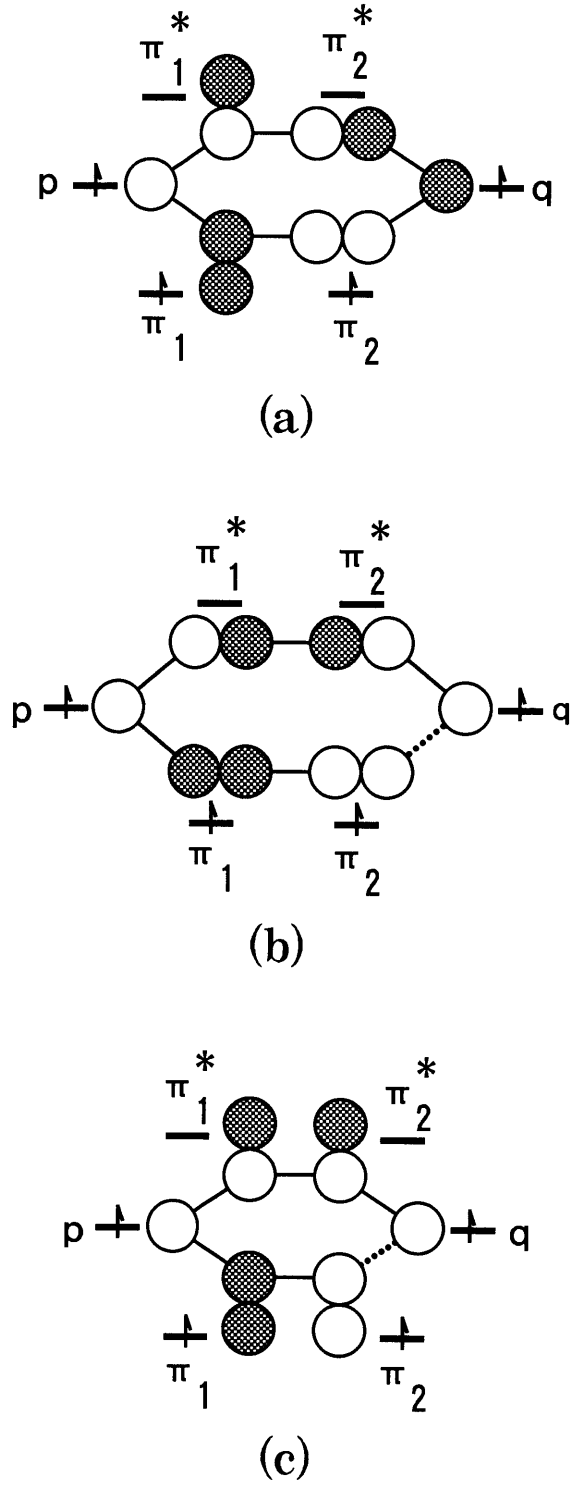
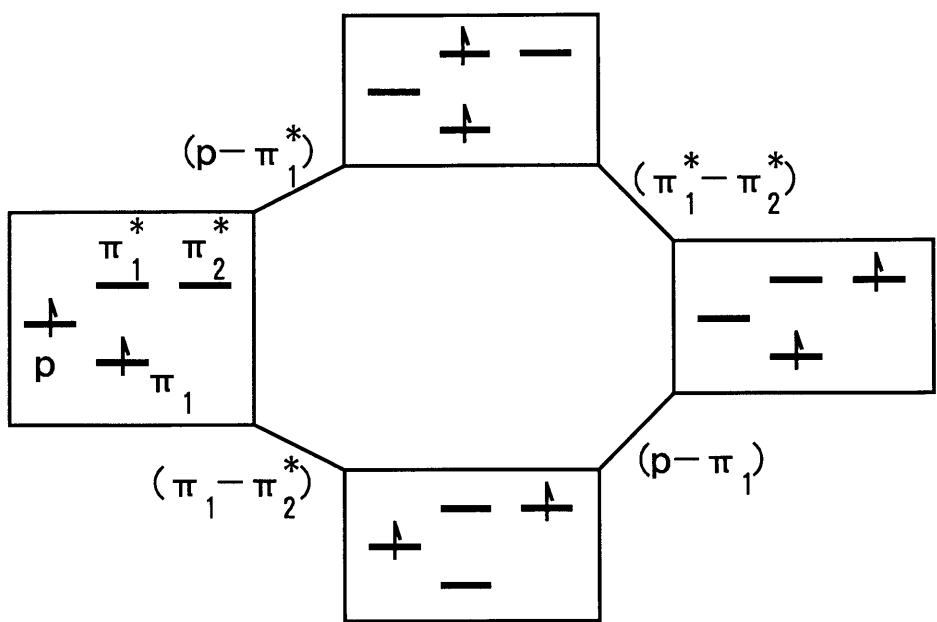
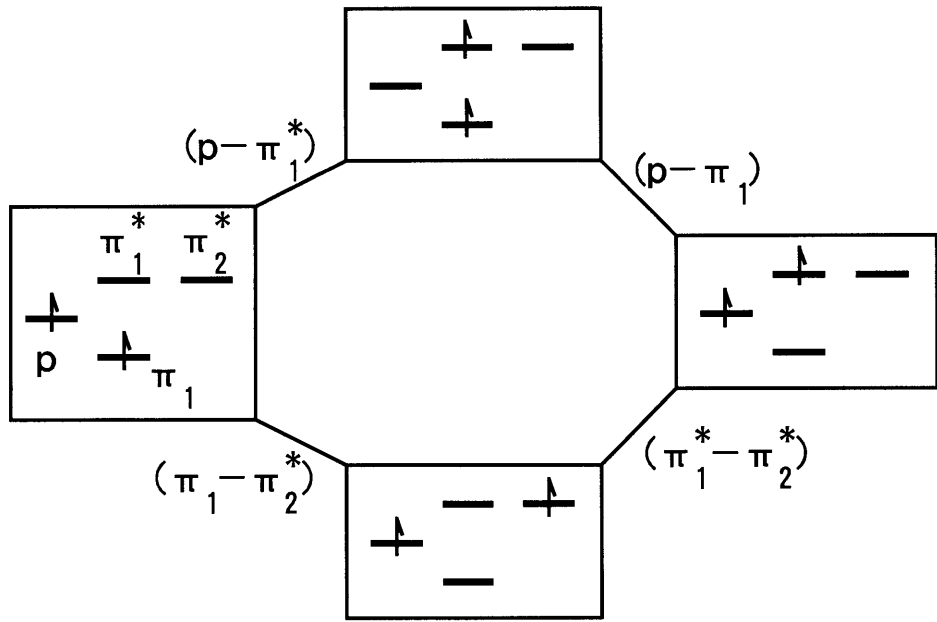


Figure 7. The orbital phase continuity of **3** (a) and the discontinuities of **4** (b) and **5** (c) for the α -spin in the triplet states.



(a)



(b)

Figure 8. The dual mechanism involving the cyclic $-\pi_1-p-\pi_1^*-\pi_2^*$ interaction in the substructure P- Π_1 - Π_2 : (a) distant delocalization of an electron from P to Π_2 and (b) polarization of Π_1 .

four-orbital interactions in the substructure $P-\Pi_1-\Pi_2$, i. e., the $-\pi_1-p-\pi_1^*-\pi_2^*$ interaction (Figure 3c) and the $-\pi_1-p-\pi_1^*-\pi_2$ interaction (Figure 3d). Let spin of an electron in the radical center P be α . The $-\pi_1-p-\pi_1^*-\pi_2^*$ interaction is involved in both of a delocalization of the α -spin electron to the distant π -bond Π_2 and a polarization of Π_1 (Figure 8). The cyclic orbital interaction plays a dual role. The another four-orbital interaction is involved in the polarization of Π_1 (Figure 9), which is not accompanied by the distant delocalization. The cyclic orbital interaction is less important. In 4 the cyclic interactions for the distant delocalization and the polarization is favored by the orbital phase continuity (Figure 10). In 5 the phase is continuous

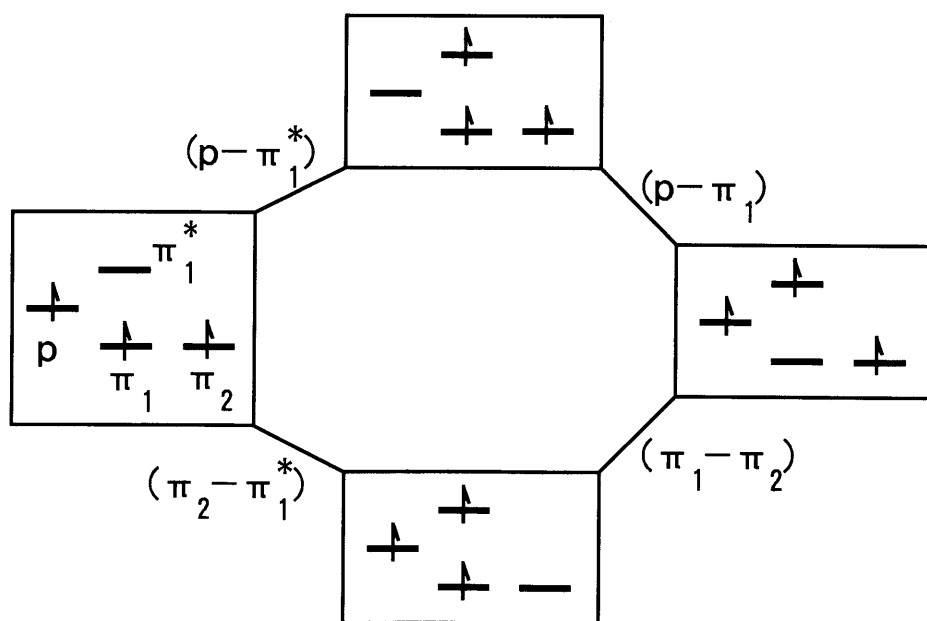


Figure 9. The mechanism of polarization of Π_1 , involving the cyclic $-\pi_1-p-\pi_1^*-\pi_2$ interaction in the substructure $P-\Pi_1-\Pi_2$.

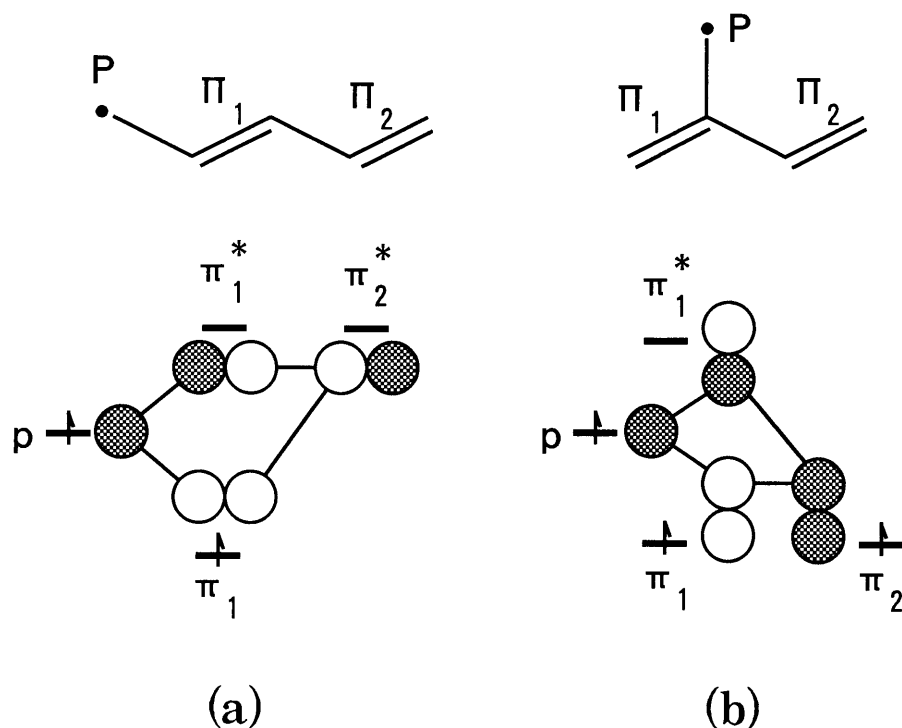


Figure 10. The orbital phase continuities of cyclic (a) $-\pi_1-p-\pi_1^*-\pi_2^*$ (4) and (b) $-\pi_1-p-\pi_1^*-\pi_2-$ (5) interactions in the substructure P- Π_1 - Π_2 .

only for the polarization. The diradical **4** is expected to be more stable than **5**. The relative stability of the C_6H_8 diradicals should decrease in the order of **3** > **4** > **5** > **6**. The prediction was supported by the MCSCF(6,6)¹⁹ calculations. The isomers **4**, **5**, and **6** are 7.3, 11.9, and 19.8 kcal/mol less stable than **3**, respectively.

In the singlet state of **3** (Figure 11a) the cyclic six-orbital interaction is disfavored by the phase discontinuity. The diradical is an unstable singlet isomer. The cyclic six-orbital interaction in **5** is favored by the phase continuity (Figure 11c). The diradical is more stable than **3**. The

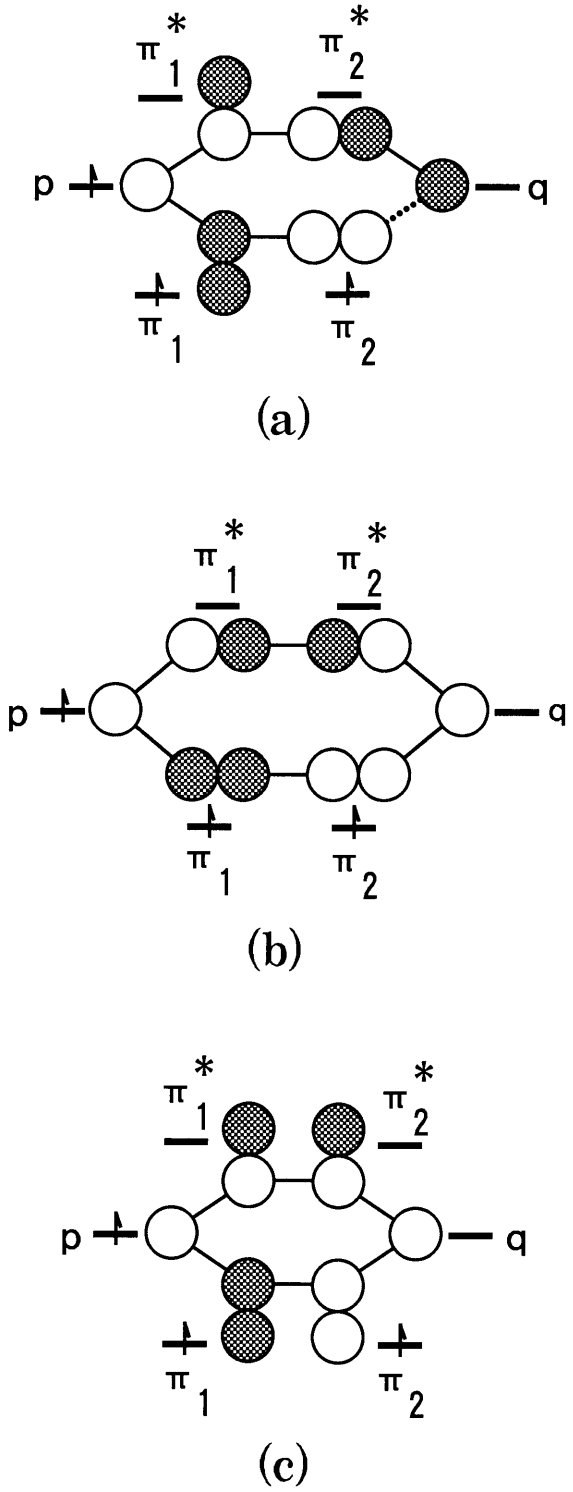


Figure 11. The orbital phase discontinuity of **3** (a) and the continuities of **4** (b) and **5** (c) for the α -spin of the singlet states.

diradicals **4** and **6** are excited states of Kekulé' molecules. The cyclic six-orbital interaction in **4** is favored by the phase continuity (Figure 11b). The diradical **6**, a P- Π -Q system, has the BD diradical unit of the phase continuity in the singlet state. The phase continuities in the diradicals of Kekulé' molecules destabilize the diradical states. The four-orbital interaction destabilizes **6** more than the six-orbital interaction does **4**. Relative stability is predicted to decrease in the order of **5** > **3** > **4** > **6**. This is consistent with the MCSCF(6,6) calculations. The diradical **5** is 3.9 kcal/mol more stable than **3**. The destabilization of the singlet diradicals of Kekulé' molecules due to the phase continuity is outstanding. Several tens kcal/mol of relative instabilities were obtained for **4** and **6**. The four-orbital interaction exhibits a greater effect than the six-orbital interaction. For **6** two low-lying excited states (2^1A_1 and 1^1B_2) were obtained. The excited states are higher in energy than that (2^1A_g) of **4**.

Xylylene Diradicals (7-9). From the resonance structures (**7-9**) and the preceding results we readily see that the relative stability of triplet states decreases in the order of **8** > **7** > **9**. The resonance structure **8** contains **3** where the cyclic six-orbital interaction is favored by the phase continuity (Figure 7a). The p-isomer **9** has a substructure **4** where the cyclic six-orbital interaction is disfavored by the phase discontinuity (Figure 7b). The diradical is an unstable triplet. The resonance structure **7** of the o-isomer contains an extended or vinylogous structure of **4**, P- Π_1 - Π_2 - Π_3 -Q, where the cyclic eight-orbital interaction is readily seen to be disfa-

vored by the phase discontinuity. The restriction by the phase discontinuity is weak in **7** relative to that in **9**. The decrease of the relative stability in the order of $8 > 7 > 9$ was confirmed by the MCSCF(6,6) calculations. The o- and p-isomer are 6.6 and 11.9 kcal/mol less stable than the m-isomer, respectively. The tendency of **7** toward a P- Π_1 - Π_2 - Π_3 -Q system was supported by the appreciably long distance (1.479 Å) between the carbons substituted by methylenes in the optimized structure.

The phase properties of singlet states are opposite to those of the triplet states. The phase is discontinuous (Figure 11a) in the resonance structure **3** contained in the diradical **8**. The diradical is not stabilized by the phase property. The phase is continuous in the resonance structure **4** and its vinylogs contained in the diradicals, **7** and **9**. The phase continuity in the diradicals of Kekulé molecules rises energies of the diradical states. The singlet diradicals **7** and **9** are destabilized by the phase continuity. The destabilization is greater in **9** since the phase continuity is higher in **4** contained in **9** than its vinylog contained in **7**. It follows that relative stability is predicted to decrease in the order of $8 > 7 > 9$. This was confirmed by the MCSCF(6,6) calculations. The m-isomer not stabilized due to the phase discontinuity were calculated to be 70 kcal/mol more stable than the lowest singlet excited states or the diradical states of the o- and p-isomers destabilized by the phase continuity. The calculations supported that the o-isomer of the low phase continuity is more stable than the p-isomer of the high continuity.

Spin Multiplicities of Ground States

The unpaired electrons of diradicals are assumed to be localized on the spatially separated radical centers in the ground configuration. Interaction of the electrons is small. Spin alignments contribute to no appreciable difference between the singlet and triplet states. The two spin states are degenerate. The electron delocalization or the polarization lifts the degeneracy. The orbital phase has been shown to control the delocalization of the unpaired electrons and the polarization. The phase continuity-discontinuity properties of the singlet and triplet states are opposite to each other. The spin preference can be predicted by the phase properties.

The diradicals of the Kekulé' molecules, **2**, **4**, **6**, **7**, and **9** have been shown to be favored by the orbital phase continuity in the singlet states. The diradicals are stabilized to be closed-shell structures, i. e., 1,3-butadiene, o-xylene, etc. The ground states of the Kekulé' molecules are the singlets.

The orbital phase is continuous in the triplet states of **1** (Figure 5a), **3** and **8** (Figure 7a). This suggests that the ground states should be triplets. This is in agreement with the experimental observations about **1**.^{21, 22} The MCSCF calculations showed that the preference of the triplet to the singlet state, ΔE_m , is 21.1 kcal/mol. The calculated C_T/C_G and C_E/C_G values showed the greater delocalization and polarization in the triplet state than those in the singlet state and supported the theory. The triplet preference of **3** and **8** is also in agreement with the previous calculations,^{16, 23} and

the experimental observations.^{24, 25} Our MCSCF calculations estimated the stabilizations (12.7 and 10.5 kcal/mol) of the triplet states of **3** and **8** relative to the singlets, respectively.

The orbital phase is continuous in the singlet state of **5** (Figure 11c). The ground state is predicted to be a singlet. In agreement with this, CI calculations²⁶ gave the ground singlet state in the planar geometry.²⁷ The present MCSCF (6, 6) calculations showed the preference (3.1 kcal/mol) of the singlet state to the triplet state.

Some theories for the spin preference have been proposed by Borden and Davidson,¹¹ by Ovchinnikov,¹² and by Radhakrishnan.¹³ The predictions about **1**, **3**, **5**, and **8** are in agreement with those by the present theories. According to Borden and Davidson, **10** is grouped into the same class as **5** where the ground states are singlet states. The phase theory gives a different prediction. The cyclic eight-orbital interaction in **10** is favored by the phase-continuity in the triplet state. The ground state should be a triplet. This was supported by the present MCSCF calculations and others.²⁹ The MCSCF(8, 8)¹⁹ calculations showed a slight (0.56 kcal/mol) preference of the triplet to the singlet state. Experimental evidence has not yet been available at this stage. The prediction of the spin preference of **10** agrees with that by Ovchinnikov and by Radhakrishnan.

The orbital phase theory can be applied to non-alternant systems, while the theories by Ovchinnikov and by Borden and Davidson were developed only for alternant systems. A non-alternant system **11** contains substructures of which the

phase properties are opposite to each other. The orbital phases are continuous in the triplet of the substructures **1** and in the singlet state of **5**, respectively. The phase continuity of the four-orbital interaction in **1** is more effective than that of the six-orbital one in **5**. The ground state is predicted to be triplet. This agrees with a result of a calculation.^{29b} The substructures **5** and **10** are both contained in **12**. The phase continuity of **5** in the singlet state is more effective than that of the eight-orbital interaction of **10** in the triplet state. The ground state is predicted to be singlet. This agrees with results of the MCSCF(6,6) calculations. The singlet ground state is 2.0 kcal/mol more stable than the triplet.

The orbital phase continuity is the most effective in the TMM substructure **1** of the non-Kekulé diradicals. The dimethylene derivatives (**13** and **14**) of triafulvene and fulvene contain the substructure. The ground states are predicted to be triplets. This is in agreement with the results of the calculations.^{16,30} The dimethylene derivatives (**15-17**) of azulene also have the TMM substructure. The prediction that the ground states are triplets were confirmed by the present MCSCF(6,6) calculations.

The Radhakrishnan's rule is applicable to the spin preference of the non-alternant systems. The orbital phase theory is applicable to both spin preference and the relative stability of isomers.

Conclusion

We developed an orbital phase theory for the open-shell electronic structures. The cyclic orbital interactions are involved in the noncyclic π -conjugated diradicals. The orbital phase continuity requirements have been derived for effective occurrence of the electron delocalization and the polarization of the π -bonds. The relative stabilities of the singlet (triplet) isomers are under control of the phase continuity-discontinuity properties of the cyclic orbital interactions. The spin preferences of the ground states of both non-alternant and alternant hydrocarbon diradicals are also controlled by the phase properties.

Appendix I

In the text the α - and β -spin parts of the determinants are separated to discuss the delocalization and polarization mechanisms. The inequalities 2 and 3 are derived by a rigid formalism shown below. Here the opposite signs of the inequalities are also explained.

The spin eigenfunctions of the triplet state with M_s (z -component of the total spin) = 1 are written as

$${}^3G = \frac{1}{\sqrt{4!}} \left| \begin{array}{ccc} \pi & \bar{\pi} & pq \\ \pi & \bar{\pi} & pq \end{array} \right|$$
$${}^3T_1 = \frac{1}{\sqrt{4!}} \left| \begin{array}{ccc} \pi & \bar{\pi} & \pi^* q \\ \pi & \bar{\pi} & \pi^* q \end{array} \right|$$

$$\begin{aligned}
{}^3T_2 &= \frac{1}{\sqrt{4!}} \left| \pi \overline{\pi} p \pi^* \right| \\
{}^3E &= x ({}^3E_1) + y ({}^3E_2) + z ({}^3E_3)
\end{aligned} \tag{a1}$$

where

$$\begin{aligned}
{}^3E_1 &= \frac{1}{2\sqrt{4!}} \left(\left| \overline{\pi} \pi^* p q \right| + \left| \pi \overline{\pi}^* p q \right| - \left| \pi \pi^* \overline{p} q \right| - \left| \pi \pi^* p \overline{q} \right| \right) + \dots \\
{}^3E_2 &= \frac{1}{2\sqrt{4!}} \left(\left| \overline{\pi} \pi^* p q \right| - \left| \pi \overline{\pi}^* p q \right| + \left| \pi \pi^* \overline{p} q \right| - \left| \pi \pi^* p \overline{q} \right| \right) + \dots \\
{}^3E_3 &= \frac{1}{2\sqrt{4!}} \left(\left| \overline{\pi} \pi^* p q \right| - \left| \pi \overline{\pi}^* p q \right| + \left| \pi \pi^* \overline{p} q \right| - \left| \pi \pi^* p \overline{q} \right| \right) + \dots \\
x^2 + y^2 + z^2 &= 1.
\end{aligned}$$

If we neglect the higher-order terms with respect to the overlaps, the overlap integrals between the configurations, S , are represented in terms of the zeroth-order terms. The configuration overlaps are then expanded in a power series in the orbital overlap integrals, s . Truncation of the series at the first-order terms gives

$$\begin{aligned}
S({}^3G, {}^3T_1) &= s(p, \pi^*) \\
S({}^3T_1, {}^3E_1) &= s(p, \pi) \\
S({}^3T_1, {}^3E_2) &= 0 \\
S({}^3T_1, {}^3E_3) &= s(p, \pi) \\
S({}^3E_1, {}^3T_2) &= s(q, \pi) \\
S({}^3E_2, {}^3T_2) &= s(q, \pi) \\
S({}^3E_3, {}^3T_2) &= 0
\end{aligned}$$

$$S(^3T_2, ^3G) = s(q, \pi^*). \quad (\text{a2})$$

The product of the overlap integrals of the cyclically interacting configurations, 3G , 3T_1 , 3E_1 , and 3T_2 is approximated to be a non-zero product of the first-order orbital overlaps

$$\begin{aligned} & S(^3G, ^3T_1)S(^3T_1, ^3E_1)S(^3E_1, ^3T_2)S(^3T_2, ^3G) \\ & = s(p, \pi^*)s(\pi^*, q)s(q, \pi)s(\pi, p). \end{aligned} \quad (\text{a3})$$

The configurations 3E_2 and 3E_3 do not participate in any cyclic interactions. Odd permutations in the Slater determinants change the signs of the right side terms in the equation a2. Whatever the permutations are, the sign of the equation a3 remain unchanged. Thus, we obtain the inequality 2. The same inequality is derived for the triplet states with $M_s = 0$ and -1 .

The spin eigenfunctions of the singlet state are written as

$$\begin{aligned} ^1G &= \frac{1}{\sqrt{2 \cdot 4!}} \left(|\pi \bar{\pi} p q| - |\pi \bar{\pi} p q| \right) + \dots \\ ^1T_1 &= \frac{1}{\sqrt{2 \cdot 4!}} \left(|\pi \bar{\pi} \pi^* q| - |\pi \bar{\pi} \pi^* q| \right) + \dots \\ ^1T_2 &= \frac{1}{\sqrt{2 \cdot 4!}} \left(|\pi \bar{\pi} p \pi^*| - |\pi \bar{\pi} p \pi^*| \right) + \dots \\ ^1E &= x(^1E_1) + y(^1E_2) \end{aligned} \quad (\text{a4})$$

where

$$\begin{aligned}
{}^1E_1 &= \frac{1}{2\sqrt{4!}} \left(\left| \overline{\pi \pi^* p q} \right| + \left| \pi \pi^* \overline{p q} \right| - \left| \overline{\pi \pi^* p} q \right| - \left| \pi \overline{\pi^* p} q \right| \right) + \dots \\
{}^1E_2 &= \frac{1}{\sqrt{12 \cdot 4!}} \left(\left| \overline{\pi \pi^* p q} \right| + \left| \pi \pi^* \overline{p q} \right| + \left| \overline{\pi \pi^* p} q \right| + \left| \pi \overline{\pi^* p} q \right| \right. \\
&\quad \left. - 2 \left| \overline{\pi \pi^* p} q \right| - 2 \left| \pi \overline{\pi^* p} q \right| \right) + \dots \\
x^2 + y^2 &= 1.
\end{aligned}$$

The overlap integrals of the configurations are approximated to the orbital overlaps

$$\begin{aligned}
S({}^1G, {}^1T_1) &= s(p, \pi^*) \\
S({}^1T_1, {}^1E_1) &= (-1) \frac{1}{\sqrt{2}} s(p, \pi) \\
S({}^1T_1, {}^1E_2) &= (-1) \sqrt{\frac{3}{2}} s(p, \pi) \\
S({}^1E_1, {}^1T_2) &= \sqrt{2} s(q, \pi) \\
S({}^1E_2, {}^1T_2) &= 0 \\
S({}^1T_2, {}^1G) &= s(q, \pi^*). \tag{a5}
\end{aligned}$$

We obtain a non-zero product of the cyclically interacting configurations:

$$\begin{aligned}
&S({}^1G, {}^1T_1) S({}^1T_1, {}^1E_1) S({}^1E_1, {}^1T_2) S({}^1T_2, {}^1G) \\
&= (-1) s(p, \pi^*) s(\pi^*, q) s(q, \pi) s(\pi, p). \tag{a6}
\end{aligned}$$

The orbital overlaps involved are the same as those in the equation a3, while the sign is opposite. No permutation in the Slater determinants changes the sign. This gives the in-

equality 3.

Appendix II

A method is presented for calculating the coefficients of bond-to-bond electron transferred configurations and bond excited configurations in a total wavefunction. The method is applicable to any spin states of molecules.

The HF type total wavefunction, Ψ , of a molecule is expanded as

$$\Psi = \sum_i C_i \Phi_i \quad (\text{a7})$$

where Φ_i is a configuration and C_i is its coefficient. The function Φ_i is constructed by Slater determinants (ϕ_{ik} ; $k = 1, 2, \dots$) so as to be a spin eigenfunction. The determinant is composed of the bond orbitals. Numbers of electrons in the orbitals are the same for the determinants belonging to Φ_i , and k runs over all permutations of electrons singly occupying the orbitals. On the other hand, the determinants are basis functions in a linear combination:

$$\Psi = \sum_{i,k} B_{ik} \phi_{ik} \quad (\text{a8})$$

where B_{ik} is a coefficient of ϕ_{ik} . Comparison of the two

equations gives

$$C_i \Phi_i = \sum_k B_{ik} \phi_{ik}. \quad (\text{a9})$$

Thus by normalizing Φ_i , we find

$$|C_i| = \left(\sum_{k,l} B_{ik} S_{ik,il} B_{il} \right)^{1/2} \quad (\text{a10})$$

where the integral between ϕ_{ik} and ϕ_{il} is denoted by $S_{ik,il}$. The equation a10 is applicable to any spin states. In the derivation an explicit expansion form of Φ_i in terms of ϕ_{ik} 's, which the Baba's method³¹ needs, is not used.

If a CI wavefunction is employed, products of B_{ik} and a CI expansion coefficient are summed up for all the CI configurations.

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Chapter 7

Unnecessary Parallelism between Kinetic and Thermodynamic Stabilities of Cyclic Conjugated Hydrocarbons: An Orbital Phase Criterion for Reactivity

Abstract: The orbital phase criteria are derived for predicting the kinetic instability of cyclic conjugated molecules. The highest intermolecular reactivities toward electron acceptors and toward electron donors results if an out of phase and in phase relation can be simultaneously assigned to all pair of neighboring bonding and antibonding orbitals of the component bonds, respectively. The thermodynamic stability is paralleled with the predicted kinetic stability for annulenes. The parallelism breaks down for the molecule with exocyclic double bonds.

The concept of aromaticity is diverse.¹ The most useful definitions for organic chemists are more or less related to the observed stability of molecules. Difficulties and confu-

sions may be encountered when we distinguish between the thermodynamic and kinetic stabilities. In principle, both stabilities are not necessarily correlated to each other though the parallelism happens to have been often observed. Thermodynamic stabilization is gained by intramolecular delocalization of electrons² while reactivity depends on intermolecular delocalization.³ A simple condition for cyclic delocalization was previously presented in terms of phase relation among the bonding and antibonding orbitals of the component bonds.⁴ That is a simultaneous satisfaction of the requirements; (1) the bonding and antibonding orbitals in phase, (2) the bonding orbital out of phase, and (3) the antibonding orbitals in phase. The derivation is based on the many-system delocalization theory, which have been successfully applied to propose the continuity-discontinuity of cyclic conjugation,⁵ cyclic orbital interaction in acyclic conjugation,⁶ and the predominance of noncyclic over cyclic manner in determining relative delocalizability of donor-acceptor disposition isomers of conjugate heterocycles.⁷ In this paper we derive an orbital phase condition for kinetic instability of cyclic conjugated molecules at the same qualitative level.

There has been noted a serious discrepancy between the calculated resonance energy and the observed stability. 3,4-Dimethylenecyclobutene (**5**) is much more stable than expected from its large negative resonance energy.⁸ The observed instability of xylylenes (**9**, **10**) is comparable with that of cyclobutadiene though the small but positive resonance energy⁹ does not suggest antiaromaticity but olefinic charac-

ter. The orbital phase requirements obtained here for intermolecular reactivity shed new light on these puzzles.

Theory

The manifold of π orbitals of a conjugated system can be formulated as linear combination of π and π^* orbitals of a double bond (Figure 1). Thus the bonding orbitals ϕ are approximated to be linear combinations of π orbitals only, and the antibonding orbitals ϕ^* are approximated to be those of π^* orbitals only. Among the bonding orbital manifold the HOMO will be the one with the largest number of out of phase (oop) combinations of the π orbitals, and among the antibonding manifold the LUMO is the one with the largest

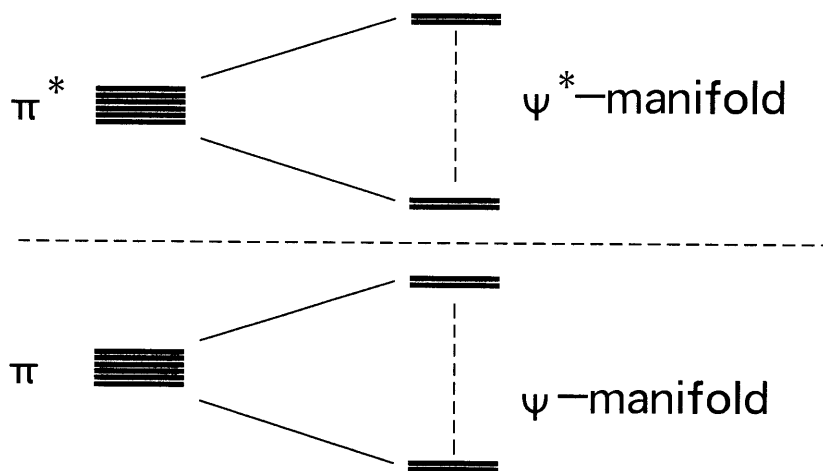


Figure 1. The bonding (ϕ) and antibonding (ϕ^*) orbital manifolds of π conjugate systems as linear combination of π and π^* orbitals of component double bonds.

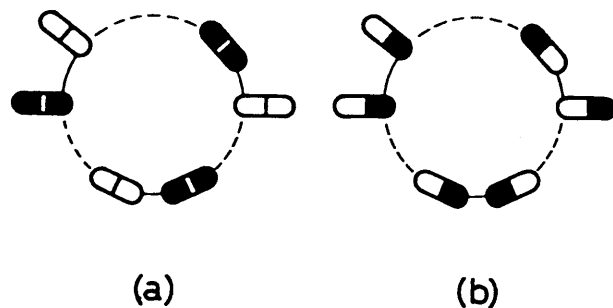
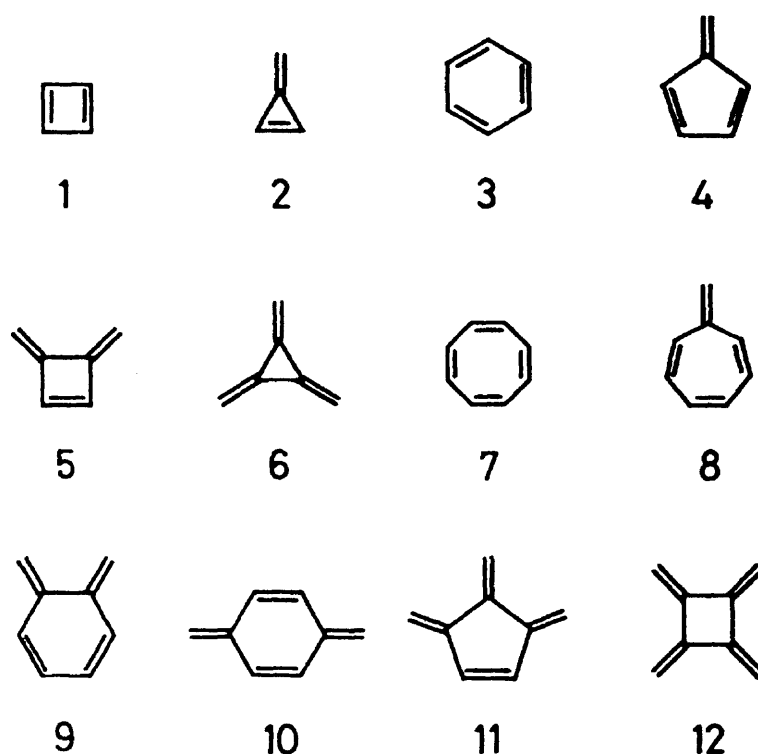


Figure 2. Out of phase combinations of bonding orbitals and phase combinations of antibonding orbitals required for highest reactivities toward electron acceptors (a) and don (b), respectively. The solid line denotes the direct interaction the neighboring orbitals.



number of in phase (ip) combinations of the π^* orbitals (Figure 2). When we try to maximize the oop combinations of the π orbitals and the ip combinations of the π^* orbitals,

the obvious rules obtain: (1) If all combinations of the π orbitals are oop, the HOMO will be the highest and the molecule is a good donor. If one combination is ip, the HOMO will be lower and the molecule is a worse donor. (2) If all combinations of the π^* orbitals are ip, the LUMO will be the lowest and the molecule is a good acceptor. If one combination is oop, the LUMO will be higher and the molecule is a worse acceptor. When we apply the rule to simple monocyclic conjugated molecules, 1-12, we can predict the kinetic instability as summarized in Table.

Table.

LUMO						
ip	2	1	2	3	2	3
oop	0	1	1	0	1	0
HOMO						
ip	0	0	1	1	1	1
oop	2	2	2	2	2	2
Acceptor	good	bad	bad	good	bad	good
Donor	good	good	bad	bad	bad	bad
LUMO						
ip	4	3	4	4	3	4
oop	0	1	0	0	1	0
HOMO						
ip	0	0	0	0	0	0
oop	4	4	4	4	4	4
Acceptor	good	bad	good	good	bad	good
Donor	good	good	good	good	good	good

More rigorous theoretical derivation of the orbital phase criterion for chemical reactivity of cyclic conjugated hydrocarbons is described in Appendix.

Discussion

Cyclobutadiene (1), which can be generated in various ways,¹⁰⁻¹² dimerizes in the argon matrix above 35 K¹¹ and exists in 2-10 ms. under the low pressure.¹² Triafulvene (2) has never been prepared.

Benzene (3) is one of the most stable organic molecules discovered in 1825 by Faraday¹³ and first synthesized in 1933 by Mitscherlich.¹⁴ Fulvene (4) first prepared by Thiec and Wiemann¹⁵ was found to be thermally unstable light yellow oil sensitive to oxygen.¹⁶ The molecule can be stored under nitrogen atmosphere at -70°C ,^{17a} but polymerizes at 20°C with half life of 3.3 hrs.^{17b} 3,4-Dimethylenecyclobutene (5) can be stored under nitrogen in the refrigerator for several days, but polymerizes rapidly upon being exposed to air.^{18a} Notable are the high boiling point (72°C ,^{18a} 51°C ^{18b}) and the high temperature (200°C)^{18c} at which the triene is quantitatively generated from 1,2,4,5-hexatetraene at low pressures. Trimethylenecyclopropane or (3)-radialene (6) is stable in dilute solution at -78°C in the absence of oxygen and in the gas phase under reduced pressure in an inert atmosphere.¹⁹ The molecule polymerizes when the vapor is warmed to room temperature or when a solution stands at 0°C .²⁰

Cyclooctatetraene (7), first synthesized by Willstätter²¹ and then in one step by Reppe²², has a nonplanar D_{2d} tub-like conformation. Heptafulvene (8) first prepared by Doering and Wiley²³ was recently isolated as a crystal at -80°C , which melts at -43°C and oligomerizes in few seconds at 20°C .²⁴ The presence of *o*-xylylene (9) as an intermediate has been inferred from the products of trapping and self-trapping reactions.²⁵ Recently, it was photochemically synthesized in ridged glass (-196°C) and was found to dimerize on melting (ca. -150°C) to the glassy solution.²⁶ *p*-Xylylene (10) was first suggested to be an intermediate in the fast flow pyrolysis of *p*-xylene at low pressure.²⁷ The molecule was then reported in a paper to only exist in gas phase and to polymerize at the moment of condensation at -190°C .²⁸ In another,²⁹ the polymerization was reported to be arrested in a frozen solution at -190°C although the half-life in solution at -78°C is about 21 hrs. Tetramethylenecyclobutane or (4)-radialene (12) is stable in dilute solution at -78°C in the absence of oxygen, but undergoes dimerization to a 1,5-octadiene on warming to room temperature.³⁰

More or less instability is common to monocyclic polyenes with exocyclic bonds, as described above. The thermodynamic origins were recently proposed to consist in the concomitant electron-delocalizing and -localizing orbital interactions in cyclic conjugation⁵ and/or in the orbital phase discontinuity in acyclic conjugation.⁶ However, no clear-cut "black-and-white" dichotomy of thermodynamic stabilities is available for monocyclic polyenes with exocyclic bonds. In

contrast, the kinetic stability is now predictable according to the unequivocal phase criterion. The kinetic stability of monocyclic polyenes with exocyclic bonds changes from a molecule to another. Some are stable toward donors and unstable toward acceptors and vice versa. The others are stable or unstable toward both reagents. Noteworthy are the stability of dimethylenecyclobutene (5) and the instability of xylylenes (9, 10) and (4)-radialene (12).

Hess and Schaad⁸ recently calculated resonance energy (RE) of a wide range of cyclic polyenes and showed an excellent correlation with the observed stabilities and chemical behaviors. However, they noted a serious failure of their method in predicting the stability of dimethylene-cyclobutene. The molecule has so large a negative RE that it should not be isolable. This is inconsistent with the experimental observation.¹⁸ The antiaromatic character was also reproduced by Aihara,^{9b} who concluded that the relative experimental stability must be ascribed to other effects than aromaticity. Now we realize that the stability is kinetic because of the low reactivity toward both donors and acceptors.

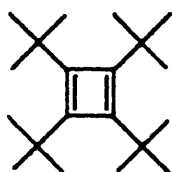
Namiot et al.³¹ determined appreciable resonance energies for o- and p-xylylenes by the Hückel molecular orbital and valence bond approaches. Coulson et al.³² and Hess and Schaad⁸ obtained results which tended to substantiate the above findings. Experimental observation^{25, 26} tends to contradict the prediction of moderate stability. The high instability is now attributed to the high reactivity toward both donors and acceptors.

The observed instability and stability unexpected from the intramolecular delocalization may be due to the inter-molecular reactivity. We can depress the reactivity by protecting a molecule against the attack of another by steric hindrance if the instability is kinetic origin. Some outstanding substituent effects on the stabilization of kinetically unstable molecules are summarized in the following from the literature.

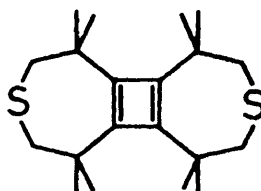
Cyclobutadiene is stabilized by *t*-butyl or similar substituents. The stability increases with the number of the substituents.³³⁻³⁵ Tetra-*t*-butyl cyclobutadiene (**13**) was quantitatively prepared even at 130°C by the thermolysis of tetra-*t*-butyltetrahedrane,³³ and was able to be subjected to the room temperature X-ray structure analysis.³⁴ Among the surprisingly stable cyclobutadiene derivatives is 3,3,7,7,10,10,14,14-octamethyl-5,12-dithiatricyclo[7.5.0.0^{2,8}]tetradeca-1(9),2(8)-diene (**14**), a yellow crystal which decomposes above 240°C.³⁶ Various attempts to prepare similar alkyl substituted methylenecyclopropenes³⁷ and even the parent compound³⁸ have not been successful until an elegant synthesis by Stang and Mangum.³⁹ They found that 1,2-dimethyl and diethyl-3-isopropylidenecyclopropenes (**15**) are remarkably stable in solution at -20°C but polymerize at room temperature and in the absence of solvent.

The 2,3,5-tri-*t*-butyl derivative (**16**) of fulvene was observed to melt at 46°C⁴⁰ at which the parent compound readily polymerizes as described above. Although simple alkyl derivatives of 3,4-dimethylenecyclobutene have not been pre-

pared,⁴¹ there are no reports which describe remarkable stabilization by the substituents. The hexamethyl derivative (17) of trimethylenecyclopropane is an extraordinarily stable crystal which melt at 131–132°C without decomposition.⁴²



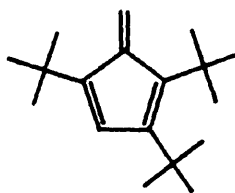
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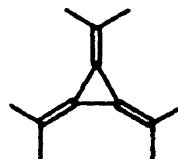
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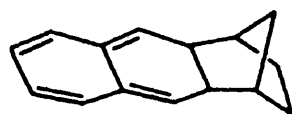
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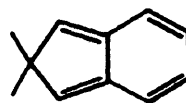
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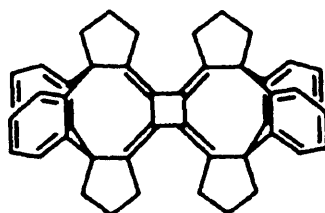
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The substituent effects on stabilization are prominent for *o*-xylylene. Among surprisingly stabilized derivatives are tricyclo[8.2.1.0^{3,8}]trideca-2,4,6,8-tetraene (18)⁴³ and 2,2-dimethylisoindene (19),⁴⁴ which are stable at room temperature in solution. A tetramethylenecyclobutane derivative (20) without any strongly perturbing atoms or groups directly interacting with the conjugated carbons does not decompose below 270°C.⁴⁵

Conclusion

A general and simple criterion for estimating the kinetic instability of cyclic conjugated molecules has been given in terms of orbital phase. The intermolecular reactivity is the highest toward electron acceptors when all pairs of the neighboring bonding orbitals of component bonds can be out of phase, and toward electron donors when all pairs of the neighboring antibonding orbitals can be in phase. This principle is applicable to heterocyclic molecules. The thermodynamic stability is completely paralleled with the kinetic stability for annulenes. The introduction of exocyclic double bond destroys the parallelism. The stability of 3,4-dimethylenecyclobutene and the instability of xylylenes, observed to be greater than expected from the resonance energy, are in agreement with the predicted kinetic stability/instability. This explanation is supported by the stabilizing effects of the bulky substituents which do not significantly perturb

the π -electronic structures. The present work suggests the observed stability/instability of cyclic conjugated molecules should be more carefully examined from the kinetic viewpoint⁴⁶ than it was done.

Appendix

Suppose that a cyclic conjugated molecule is composed of localized bonds, A, B, ..., Y and interact at A with an external entity, Z, as is shown in Figure 3. The mechanism of electron delocalization among many systems or bonds were previously proposed and successfully applied to reveal some unprecedented aspects electron delocalization.⁵⁻⁷ The delocalization mechanism is applied here to kinetic instability of cyclic conjugated molecules.

The mechanism of delocalization is illustrated for an electron accepting Z in Figure 3a. An electron shifts from the bonding orbital of A, a , to the LUMO of Z, z^* through $a-z^*$ orbital interaction. This is the predominant part of the interaction between the ground state configuration, $\Phi(G)$, and the electron transferred configuration, $\Phi(a \rightarrow z^*)$. The electron shift leaves an electron hole in a . Then the hole accepts an electron from neighboring bonding orbital b through the $a-b$ orbital interaction or through the $\Phi(a \rightarrow z^*)-\Phi(b \rightarrow z^*)$ configuration interaction. The resulting hole in b is in turn supplied with an electron by c , similarly through the $b-c$ orbital interaction or through $\Phi(b \rightarrow z^*)-\Phi(c \rightarrow z^*)$

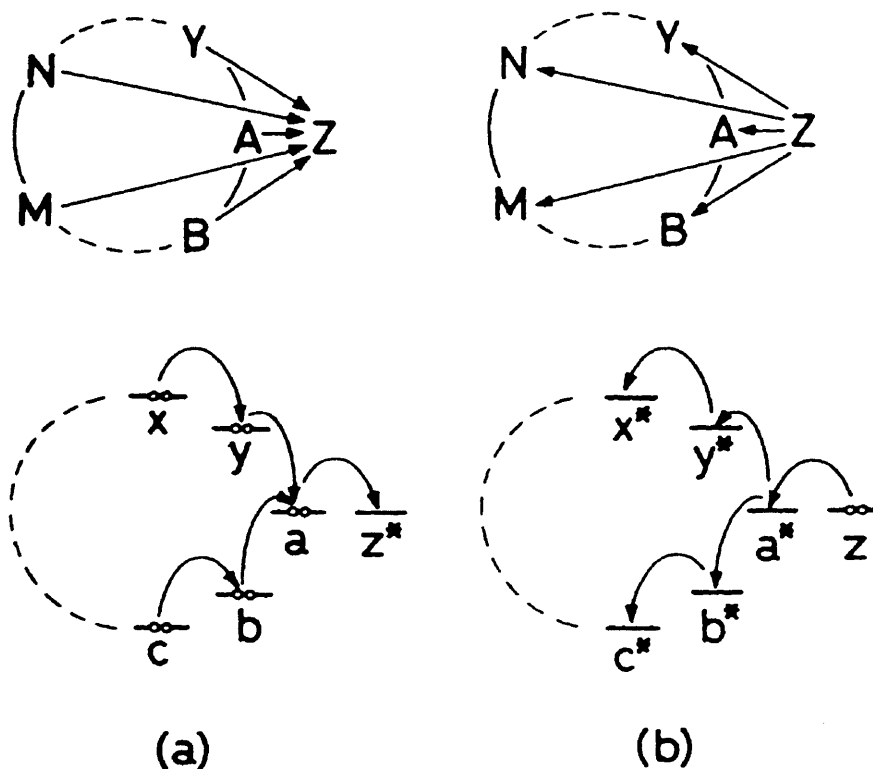


Figure 3. Mechanism of electron delocalization in cyclic conjugated molecules interacting with an acceptor (a) and with a donor (b), in terms of electron configurations (top) and orbitals (bottom).

configuration interaction. Thus, an hole migrates farther away from A, as well as in the opposite direction via A, Y, X and so on.

An analogous mechanism for an electron-donating Z is shown in Figure 3b. An electron transfers from Z to A through the $z-a^*$ orbital interaction or through the $\Phi(G)-\Phi(z \rightarrow a^*)$ configuration interaction. The electron accepted in a^* then shifts to b^* through the a^*-b^* orbital interaction or through the $\Phi(z \rightarrow a^*)-\Phi(z \rightarrow b^*)$ configuration interaction. The electron in turn migrates to c^* , d^* , etc. through the in-

interactions between the antibonding orbitals or between the transferred configurations. Such electron shift also take place in the opposite direction via Y, X, and so on.

The condition for electron delocalization was previously shown to be given by the sign of product, P, of overlap integrals between configurations, S, i. e.,

$$P > 0 \quad (1)$$

where:

$$P(Z=\text{acceptor}) = S(G/a \rightarrow z^*) S(a \rightarrow z^*/b \rightarrow z^*) \\ \times \dots \times S(y \rightarrow z^*/a \rightarrow z^*) S(a \rightarrow z^*/G) \quad (2)$$

and:

$$P(Z=\text{donor}) = S(G/z \rightarrow a^*) S(z \rightarrow a^*/z \rightarrow b^*) \\ \times \dots \times S(z \rightarrow y^*/z \rightarrow a^*) S(z \rightarrow a^*/G) \quad (3)$$

The ground state and transferred configurations can be written in an unified manner without loss of generality as:

$$\Phi(G) = \frac{1}{\sqrt{N!}} |a \bar{a} b \bar{b} \dots y \bar{y} z \bar{z}|, \\ \Phi(i \rightarrow z^*) = \frac{1}{\sqrt{2N!}} (|a \bar{a} b \bar{b} \dots i \bar{z}^* \dots y \bar{y} z \bar{z}| \\ + |a \bar{a} b \bar{b} \dots z \bar{i}^* \dots y \bar{y} z \bar{z}|), \\ \Phi(z \rightarrow i^*) = \frac{1}{\sqrt{2N!}} (|a \bar{a} b \bar{b} \dots i \bar{i} \dots y \bar{y} z \bar{i}^* |$$

$$+ \left| a \bar{a} b \bar{b} \dots i \bar{i} \dots y \bar{y} i^* \bar{z} \right|$$

where N is the number of electrons. The approximation of each configuration overlap integral as a single orbital overlap integral, s , then yield a unique sign property:

$$S(G/i \rightarrow z^*) \sim \sqrt{2}s(i/z^*), \quad (4a)$$

$$S(G/z \rightarrow i^*) \sim \sqrt{2}s(z/i^*), \quad (4b)$$

for I adjacent to Z while otherwise neglected, and:

$$S(i \rightarrow z^*/j \rightarrow z^*) \sim -s(i/j), \quad (5a)$$

$$S(z \rightarrow i^*/z \rightarrow j^*) \sim s(i^*/j^*), \quad (5b)$$

for I and J adjacent to each other while otherwise neglected. From Equation 4 and 5, Equation 2 and 3 are rewritten as:

$$P(Z=\text{acceptor}) = 2(-1)^n s(a/z^*)^2 s(a/b) s(b/c) \\ \times \dots \times s(x/y) s(y/a) \quad (6)$$

$$P(Z=\text{donor}) = 2s(z/a^*)^2 s(a^*/b^*) s(b^*/c^*) \\ \times \dots \times s(x^*/y^*) s(y^*/a^*), \quad (7)$$

where n is the number of the adjacent bond pairs. The overlap integral between Z and A appears twice in the product so that there is no effect on the sign of P . The sign of P depends on the phase relation among the bonding orbitals in the

cyclic conjugated molecules for an electron accepting Z. As Equation 5a suggests, an out-of-phase combination ($s < 0$) of any pair of adjacent bonding orbitals satisfies Inequation 1. For an electron donating Z, Equation 5b similarly suggests that an in phase combination ($s > 0$) between any pair of adjacent antibonding orbitals satisfies Inequation 1. Cyclic conjugated molecules are reactive or kinetically unstable toward electron acceptors when all pairs of neighboring bonding orbitals can be out of phase, and so toward electron donors when all pairs of neighboring antibonding orbitals can be in phase (Figure 2).

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Concluding Remarks

Thermodynamic stabilities of a variety of noncyclic closed-shell molecules were successfully predicted by the orbital phase theory. The orbital phase is continuous in the cross conjugated ($4n+2\pi$ electrons/ $4p$ orbitals) systems and in the linear ($4n/4p$) conjugations. Interestingly, the dependence of the stabilities of the cross and linear conjugations on the number of electrons is similar to that of the Hückel and Möbius conjugations of the cyclic polyenes. The orbital phase theory was shown to be applicable to metal or coordination chemistry. Tricoordinated metal complexes with abnormally acute ligand-metal-ligand angles were designed.

An orbital phase theory was developed for open-shell electronic structures. The requirements for the orbital phase continuity were derived: (1) electron donating orbitals out of phase, (2) accepting orbitals in phase, and (3) donating and accepting orbitals in phase. Both radical orbitals in triplet states of diradicals are donating or accepting, while one of the orbitals is donating, the other being accepting in singlet diradicals. The theory was applied to π -conjugated diradicals. Thermodynamic relative stabilities of the isomers were successfully predicted. Furthermore, the theory was

shown to be useful in predicting the spin multiplicities of the ground states of not only alternant but also non-alternant diradicals.

Kinetic instabilities of cyclic polyenes toward electron donors and acceptors were predicted by the orbital phase theory. The instabilities were shown to be parallel to thermodynamic one for the polyenes with only endocyclic double bonds, while the parallelism does not necessarily hold for the polyenes with exocyclic double bonds.

For designing molecules or chemical reactions the orbital phase theories have been shown to be powerful in predicting the stabilities of noncyclic systems as well as the cyclic ones, and those of the open-shell electronic systems as well as the closed-shell ones. The orbital phase properties may have more important roles in chemistry than we know at the present.

List of Publications

- Chapter 1 *J. Chem. Soc. Perkin Trans. 2* **1984**, 2019.
Chapter 2 *Bull. Chem. Soc. Jpn.* **1985**, 58, 601.
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Chapter 4 *Chem. Lett.* **1994**, 1601.
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